Low-Power Decoupling Sequences for High-Resolution Chemical-Shift and Local-Field NMR Spectra of Liquid Crystals*

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Various new and well-established multiple-pulse sequences that provide homonuclear dipolar decoupling are compared on a high-resolution spectrometer/probe configuration using low RF-irradiation powers. Proton–proton decoupled carbon-13 spectra of singly ^{13}C-labeled benzene dissolved in a nematic liquid crystal and of the liquid crystal I52 are presented. Two classes of multiple-pulse sequences are studied that produce either broadband decoupled carbon spectra or separated local-field spectra. Several new approaches for the design of windowless sequences are demonstrated to be valuable in these heteronuclear experiments. They include implementations of the iterative MLEV scheme and the use of 270° pulses. Furthermore, non-cyclic propagators have been found that exhibit advantages over closely related cyclic analogues in both classes of decoupling sequences. © 1995 Academic Press, Inc.

INTRODUCTION

In a recent publication (*1*) we presented proton-detected separated local-field spectra of liquid-crystalline samples measured in a high-resolution probe equipped with a saddle coil using a "liquid-state" low-power spectrometer. The experiments were successful in resolving long-range heteronuclear dipolar couplings, but despite good tune-up behavior, the resolution was limited to about 20 Hz. We have therefore investigated multiple-pulse sequences for dipolar decoupling at the low RF-irradiation powers required on our present high-resolution setup. Low-power decoupling is of prime importance to avoid sample heating in liquid-crystalline samples (*2*).

To date, most dipolar decoupling sequences feature time periods without RF irradiation (windows), either because direct observation of the time evolution is necessary, as in imaging experiments (*3*), or because of the well-known stability of cycles like MREV-8 (*4, 5*). However, fully windowless sequences may exhibit significant advantages (*6*), in particular when low RF-field strengths are required. Examples of windowless sequences are the BLEW sequences

(*6*), the WIM-24 sequence (*7*), and the COMARO sequences (*8*).

In this paper we describe and experimentally verify some practical approaches that were found to display advantages over established sequences. The performance of the sequences was tested on a sample with comparatively small dipolar couplings (^{13}CC$_5$H$_6$ in a nematic solvent), and the same sequences were applied to a sample of the liquid crystal I52 (*9*) with dipolar couplings that are large compared to the B_2 field strength. Current work on analytical calculations and numerical simulations should provide further theoretical understanding of the findings that might allow improvements of the decoupling sequences.

GENERAL CONSIDERATIONS

Among the areas of nuclear magnetic resonance in which multiple-pulse sequences have been developed and successfully applied are broadband heteronuclear J decoupling in isotropic liquids (*10, 11*) and homonuclear dipolar decoupling in solids and liquid crystals (*12, 13*). Among the latter, which are commonly discussed in the framework of average Hamiltonian theory (*12*), there are two fundamentally different types of sequences: one type removes the bilinear homonuclear dipolar couplings while retaining the linear interactions between the irradiated spins and heteronuclei or static fields, thus allowing the determination of chemical-shift tensors (*14*) and heteronuclear dipolar coupling constants (*15, 16*). The other sequences not only remove the bilinear terms but also the linear interactions and are used in solid-state imaging (*3*), broadband heteronuclear decoupling (*8*), and cross-polarization experiments (*7*). Such sequences have been called *isotropic* sequences (*7*).

Most sequences used in isotropic liquid phases are obtained by an *iterative expansion* of basic cycles to "super-cycles" that correct errors accumulated during the irradiation of the basic cycle period. Up to a certain stage of recursion these expansion schemes work very well and represent a powerful tool for the design of multiple-pulse sequences. An iterative scheme based on a direct solution of the equation

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of motion (*17*), as well as the MLEV expansion scheme (*10*), relies on combinations of pulse trains with identical fragments that are phase shifted by 180°.

Most of the homonuclear dipolar decoupling sequences consist of 90° pulses, and decoupling is achieved by rotating the toggling frame (*12*) about the magic angle with the static magnetic field. Here, the pulse phases cannot be restricted to two values separated by 180° and, in practice, sequences with orthogonal pulse phases have been found to be superior to other possible implementations (*18*). Inversion of a pulse-train fragment, i.e., an application of the same pulses in reversed order and with inverted pulse phases, has been as useful a concept as phase shifts of 180°. The main effort in the development of homonuclear dipolar decoupling sequences has been put into cycles that retain scaled linear interactions, such as WHH-4 (*14*), MREV-8 (*5*), BR-24 (*19*), and the windowless BLEW sequences (*6*). Such sequences all consist of 90° pulses with orthogonal phases. Among the windowless variants of the isotropic sequences, WIM-24 (*7*) and the COMARO sequences (*8*) have been designed for heteronuclear cross polarization and for heteronuclear decoupling, respectively. Whereas WIM-24 employs simple 90° pulses, COMARO consists of composite 90° pulses that are less prone to pulse errors and offset effects.

Windowless Cycles with Only 90° Pulses

In the following discussion, a train of pulses that leads the toggling frame through a cycle after *n* repetitions will be called a (1/*n*) *propagator*. In this terminology, cyclic sequences are (1)-propagators. The scaling factor for the linear interactions of a cycle that consists of *n* repetitions of a (1/*n*)-propagator will be called the *intrinsic* scaling factor of the given propagator; cycles with vanishing scaling factors achieve heteronuclear decoupling. Arbitrary sequences containing only 90° pulses with orthogonal phases will be cyclic in the toggling frame after a maximum of four repetitions. Any such sequence necessarily rotates the frame back to its original state (*n* = 1), by 90° (*n* = 4) or by 180° (*n* = 2) about one of the three coordinate axes, by 180° (*n* = 2) about one of the six coordinate-plane diagonals, or by 120° (*n* = 3) about one of the four space diagonals in the magic angle with *z* (Fig. 1). In our heteronuclear local-field experiments it often proved more efficient to repeat a basic sequence to its cyclic stage rather than combine it with its inversion. In most cases, sampling of the signal is convenient only after all of the *n* repetitions. Since the sampling rate is always a crucial factor when pulses of long duration are used, short propagators are preferable over longer ones. For homonuclear dipolar decoupling to be achieved, the propagators must be selected with some care.

A concise description of the average Hamiltonian treatment for cycles consisting of 90°-pulse trains with finite lengths can be found in Ref. (*6*). In particular, two rules were established that allow a straightforward design of se-
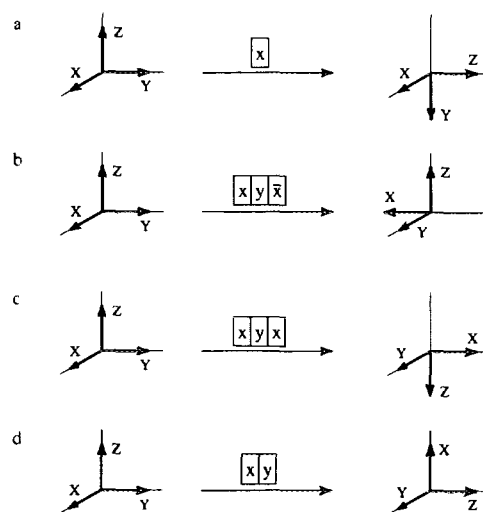

FIG. 1. Effect of various pulse groups on the toggling-frame Z state. The boxes represent 90° RF pulses with the indicated phase. The bar above a given pulse phase denotes a phase shift of 180°. The pulse sequences achieve net rotations in spin space of 90° about a coordinate axis (a, b), of 180° about a coordinate-plane diagonal (c), or of 120° about a space diagonal in the magic angle with z (d). The left-handed rotations are in agreement with conventions in earlier work on multiple-pulse sequences (*12*). All four pulse groups return the toggling frame back to its original Z state after a few repetitions. They represent (1/4), (1/4), (1/2), and (1/3) propagators, respectively. Upon repetition to cyclicity sequences, (b), (c), and (d) comply with rule (A) for homonuclear dipolar decoupling.

quences with a vanishing zero-order homonuclear dipolar-coupling Hamiltonian: (A) Each of the pulses should rotate the toggling frame (*12, 20*) from a state $\pm \alpha$ to a state $\pm \beta$, where α and β denote X, Y, or Z. The first rule requires that the time-averaged squares of the projections of the rotating-frame z axis on the X, Y, and Z axes of the toggling frame be equal. In a realization with orthogonal 90° pulses, this is accomplished when the toggling frame states X, Y, and Z, with either sign, occur with equal probability during the pulse sequence. Such sequences accomplish successive net rotations of the toggling frame about the space diagonals that span the magic angle with the z direction parallel to the external field. (B) For every transition of the toggling frame $\alpha \rightarrow \beta$ there should occur a similar transition $\alpha \rightarrow -\beta$, $-\alpha \rightarrow \beta$, $\beta \rightarrow -\alpha$, or $-\beta \rightarrow \alpha$ (α, $\beta = X$, Y, Z). This restriction results from the evolution of the coupling during the finite pulse widths. Sequences that comply with these two rules achieve homonuclear dipolar decoupling in the zero-order approximation.

EXPERIMENTAL

The spectra presented were measured on a Bruker AM-400 WB spectrometer with a commercial "inverse" 5 mm probe equipped with two saddle coils. The inner coil is tuned to 400.13 MHz and the deuterium frequency whereas the

outer coil is tunable to a heteronucleus frequency. The two samples used were singly labeled benzene ($^{13}C\text{-}C_5H_6$) oriented in the liquid crystal EK-11650 (Kodak Eastman) and the pure liquid crystal I52. For the carbon-13 spectra, a B_2 field of 21 kHz was used for the ^1H irradiation. The aquisition times were 0.2 s for the benzene and 0.1s for the I52 sample. Two hundred fifty-six scans were coherently added for the I52 spectra, whereas only one scan was acquired at each decoupler offset for the benzene spectra. No window multiplications were applied to the FID prior to Fourier transformation. No attempts were made to synchronize the sampling of the ^{13}C signal with the multiple-pulse train on the proton channel. For the benzene spectra, the parameters for each sequence were optimized under on-resonance conditions and used without change to study off-resonance behavior. All experiments were repeated several times over a period of months. For each experiment, approximately the same amount of time was spent on optimizing the pulse-sequence parameters. The results were found to vary significantly with some sequences, especially some of those that retain linear interactions, producing large variations, as described below.

ISOTROPIC SEQUENCES

Heteronuclear decoupling in solid and liquid-crystalline samples is commonly achieved by high-power cw irradiation. For the case of static samples with more than one chemical-shift frequency and homonuclear dipolar couplings comparable to the B_2 field strength, however, multiple-pulse sequences should provide better heteronuclear dipolar decoupling than cw irradiation (8, 21). Designed to remove both linear and bilinear terms, the same sequences can also be employed for heteronuclear decoupling of spin-1 nuclei subject to quadrupolar interactions (8). Furthermore, cross polarization by the simultaneous application of such a sequence to both nuclei is less sensitive to deviations from the Hartmann–Hahn condition than cw spin-lock experiments (7, 22, 23). A corresponding iterative expansion scheme should not only take linear interactions into account but also bilinear homonuclear dipolar couplings. Here, we present a direct adaptation of the MLEV scheme and show that, although the recursive expansion is not generally expected to improve homonuclear dipolar decoupling, the resulting sequences achieve efficient heteronuclear dipolar decoupling. Like the original MLEV sequences (24), our new sequences consist of composite inversion elements R that are combined according to the rules, the MLEV-4 and MLEV-16 cycles being given by the following expressions:

$$R_2\bar{R}_2 \qquad [\text{MLEV-4}]$$

$$R_2\bar{R}_3R_2\bar{R}_3R_3\bar{R}_2R \qquad [\text{MLEV-16}]$$

$$(R_2 = RR, R_3 = RRR, \text{etc.}).$$

In order to account for the homonuclear dipolar couplings, we worked with the inversion elements displayed in Fig. 2, which have already been used in a range of different contexts (25–28).

MLEV-analogous sequences constructed with the elements of Figs. 2a, 2b, and 2c comply with rule (A) for homonuclear dipolar decoupling. However, in each element R there occurs a transformation that is not compensated in the sense of rule (B). There are two obvious ways to extend such a sequence in order to comply with rule (B): (i) Combine it with the same sequence where either the phase of all the y pulses or the phase of all the x pulses is shifted by 180°; this results in sequences that are very similar to WIM-24. (ii) Combine it with the same sequence where all the phases are shifted by 90°. On our spectrometer and with the benzene sample this second variant proved more successful. The relative magnitude of bilinear and linear interactions determines the stage of the expansion at which such a phase shift is more efficient than a further extension according to the MLEV scheme. If 270° pulses (Fig. 2b) instead of 90° pulses (Fig. 2a) are employed, the violations of rule (B) per unit time are reduced by a factor of three. The use of composite 90° pulses, e.g., those employed in the COMARO sequences (Fig. 2c), results in comparable improvements.

It also seems promising to work with inversion elements that comply with rules (A) and (B) and therefore already achieve homonuclear dipolar decoupling to the zero-order approximation. Examples of propagators that meet this con-
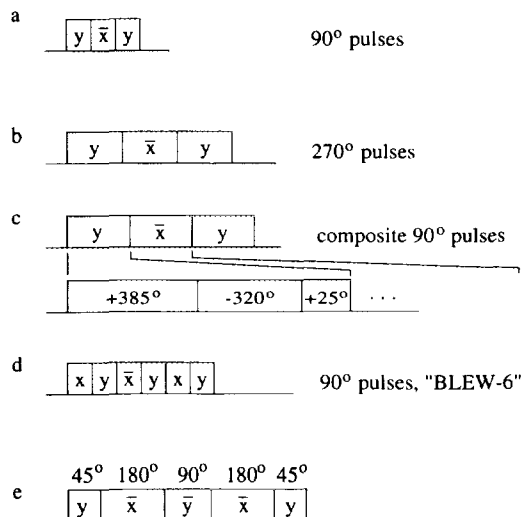
FIG. 2. Composite inversion pulses R used in this work. The simplest variant consists of three 90° pulses where the central pulse is applied with a phase difference of 90° relative to the phase of the flanking pulses (a). A trivial but significantly better performing variant of this scheme is obtained by replacing the 90° pulses with 270° pulses (b). Alternatively, the 90° pulses themselves can be implemented as better self-refocusing composite pulses (c). Other inversion elements, which have been developed in different contexts, already achieve homonuclear dipolar decoupling in zero-order approximation (d, e).
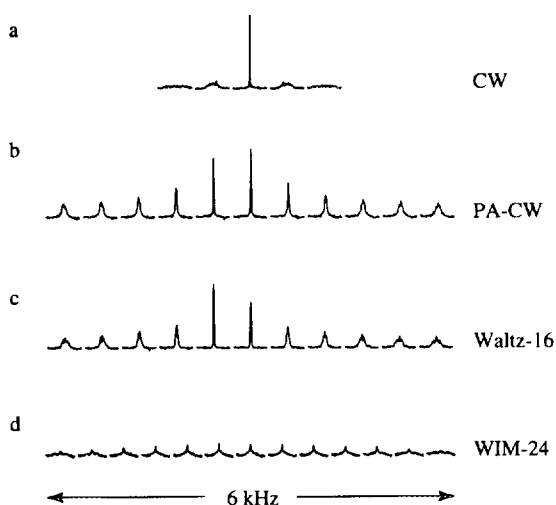
FIG. 3. $^{13}C\{^1H\}$ spectra of singly ^{13}C-labeled benzene oriented by a liquid-crystalline matrix, measured with different proton-irradiation schemes and ^1H-decoupler offsets. The offset was incremented in 500 Hz steps from right to left. The spectra were obtained by irradiating the protons with (a) a continuous wave, (b) a phase-alternated continuous wave (phase changes of 180° after every 300 μs), (c) the WALTZ-16 decoupling scheme, and (d) the ^1H part of the isotropic mixing sequence WIM-24.

offset range of approximately ±5 kHz (COMARO-2) (Fig. 4a) and ±6.5 kHz (COMARO-4) (Fig. 4c). However, the signal intensity for on-resonance decoupling reached only about 75 to 90% of that in the cw decoupled spectrum. This proved to be true for all the composite-pulse decoupling schemes that we tested. COMARO-2, which was originally used for ^2H decoupling, consists of composite 90° pulses with orthogonal phases given by

$$(yx)_3 \, (\bar{y}x)_3. \qquad\qquad [\text{COMARO-2}]$$

Each of these composite 90° rotations consists of a 385°, −320°, and 25° pulse. By choice of different pulse phases, the same composite pulses may be grouped into the inversion elements displayed in Fig. 2c. The MLEV-4 analogue constructed with these elements contains the same number of pulses as COMARO-2 and was found to decouple over a marginally wider decoupler-offset range than COMARO-2 (Fig. 4b). Although the sequences that employ the 90° pulse inversion elements of Fig. 2a were found to achieve continuously better decoupling upon expansion up to the MLEV-16 analogue and were more successful than WIM-24, they
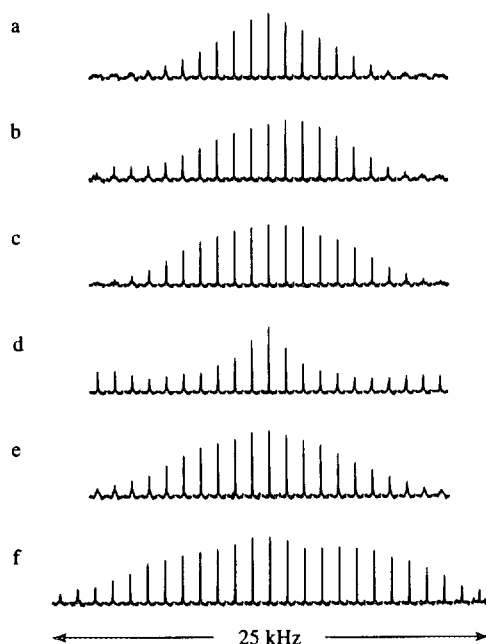
dition are the three different six-pulse groups that have been developed for the BLEW sequences. Among these, the pulse group used in the original BLEW-12 sequence (Fig. 2d) exhibits a vanishing intrinsic scaling factor and also compensates best for RF inhomogeneity (27). An interesting alternative that yielded exceptionally good results in preliminary simulations with two-spin systems and also performed well experimentally is the five-pulse inversion element (25) (Fig. 2e).

Figure 3 compares $^{13}C\{^1H\}$ spectra of singly ^{13}C-labeled benzene oriented by a liquid crystal. They were measured with different proton-irradiation schemes and decoupler offsets. Whereas cw irradiation (Fig. 3a) provided the best decoupling of all decoupling schemes under on-resonance conditions, it exhibited extremely poor off-resonance properties. By shifting the phase of the B_2 field periodically by 180° (Fig. 3b), some improvement in the bandwidth was observed. WALTZ-16 (29), which is one of the most popular heteronuclear decoupling sequences in isotropic liquid samples, was not very successful at dipolar decoupling (Fig. 3c)— presumably because it fails to average out homonuclear proton–proton couplings. WIM-24 (7), designed for heteronuclear cross polarization in the presence of homonuclear dipolar couplings, was found to achieve rather imperfect heteronuclear decoupling (Fig. 3d). It consists of 90° pulses with the pulse phases

$$(\bar{y}x\bar{y})_2 \, (yxy)_2 \, (\bar{y}\bar{x}\bar{y})_2 \, (y\bar{x}y)_2. \qquad [\text{WIM-24}]$$

In contrast, the COMARO sequences (8), which were designed for heteronuclear decoupling, worked well within an

FIG. 4. $^{13}C\{^1H\}$ spectra of singly ^{13}C-labeled benzene oriented by a liquid crystal measured with different proton-irradiation schemes and ^1H-decoupler offsets. In contrast to Fig. 2, the decoupler offset was incremented in 1 kHz steps from right to left. Spectra in (a) and (c) were measured with the original COMARO-2 and COMARO-4 sequence, respectively. In (b) the MLEV-4-analogous sequence constructed with the same composite 90° pulses as in COMARO was used. The decoupling sequence of (d) is the MLEV-4 analogue constructed with the inversion elements of Tycko et al. (25) (sequence [4]). (e) and (f) display spectra measured with a decoupling scheme that combines three 270° pulses into inversion elements R (sequences [1] and [2], respectively).
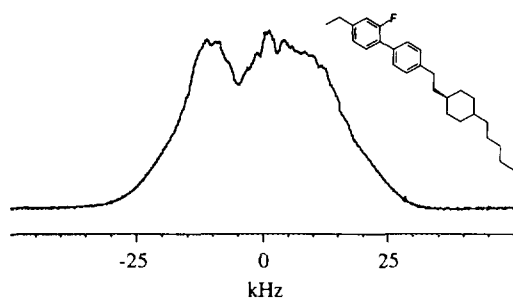
FIG. 5. ^1H spectrum and structural formula of the liquid crystal I52. For the $^{13}C\{^1H\}$ spectra, the decoupler frequency was placed in the center of the ^1H spectral band. The full width at half-maximum of the band is about 36 kHz.

performed significantly worse than COMARO-2. This is not true, however, for the sequences constructed with the 270° pulse elements. We found the off-resonance characteristics of the 96-pulse cycle that consists of two MLEV-16 analogous sequences shifted by 90°,

$$(R_2\bar{R}_3R_2\bar{R}_3R_3\bar{R}_2R)(R'_2\bar{R}'_3R'_2\bar{R}'_3R'_3\bar{R}'_2R')$$

$$(R = (y\bar{x}y),\ R' = (\bar{x}\bar{y}\bar{x})),\ 270°\ \text{pulses,}\quad [1]$$

to compare favorably with COMARO-2 (Fig. 4e). The pulse train with the broadest offset range for the benzene sample, however, was a noncyclic (1/2) propagator derived from this 96-pulse cycle (Fig. 4f):

$$\{(R_2\bar{R}_3R_2\bar{R}_3R_3\bar{R}_2R)\ (R'_2\bar{R}'_3R'_2\bar{R}'_3R'_3\bar{R}'_2R')R\}_2\ \bar{R}$$

$$(R = (y\bar{x}y),\ R' = (\bar{x}\bar{y}\bar{x})),\ 270°\ \text{pulses.}\quad [2]$$

We mention that the performance of the basic MLEV-16-analogous cycle with either 90° pulses or 270° pulses was also improved by a phase change of its last pulse by 90°, with the sign of the change being crucial (y to x). The resulting 48-pulse propagator leads the toggling-frame states through the permutations $(X,\ Y,\ Z) \rightarrow (Z,\ -X,\ -Y) \rightarrow (-Y,\ -Z,\ X) \rightarrow (X,\ Y,\ Z)$, and thus represents a (1/3) propagator with a cycle length corresponding to 144 pulses. The most successful cycle we found with the BLEW-6 inversion element (Fig. 2d) was

$$(xy\bar{x}yxy)_2\ (\bar{x}\bar{y}x\bar{y}\bar{x}\bar{y})_2\ (yxy\bar{x}yx)_2\ (\bar{y}\bar{x}\bar{y}x\bar{y}\bar{x})_2.\quad [3]$$

However, the decoupler-offset range of this cycle on the benzene sample was only about ±2.5 kHz and the resolution of the I52 spectra was lower than that obtained with other decoupling sequences (compare below). In contrast, the MLEV-4 analogue with the inversion elements of Fig. 2e,

$$R_2\bar{R}_2,\quad R = 45°_y\ 180°_x\ 90°_y\ 180°_x\ 45°_y,\quad [4]$$

was found to decouple the benzene sample over a very wide offset range but to produce broad lines at medium decoupler offsets (Fig. 4d).

I52 Spectra

The proton spectrum of unlabeled I52 is shown in Fig. 5. Its spectral width exceeded the strength of our decoupling field by a factor of almost two. This ratio was even more unfavorable in the case of the ^{13}C isotopomers. Figure 6 displays ^{13}C spectra obtained with different decoupling schemes. Overall, the cw, WIM-24, and Waltz-16 spectra displayed a lower resolution than the spectra obtained with the other multiple-pulse sequences. The information content in the spectra produced by COMARO-2 and by sequences [1] and [4] was comparable (Figs. 6e–6g), while phase-alternated cw performed slightly worse (Fig. 6b). Although the overall performance of cw decoupling was poor compared to that of the multiple-pulse sequences, the corresponding spectrum (Fig. 6a) displayed signals in the high-frequency end of the aliphatic region which were almost completely absent in all the spectra measured with multiple-pulse decoupling or even phase-alternated irradiation. We note that in the multiple-pulse spectra there are five sharp peaks in the aliphatic region which we tentatively assign to the two methyl groups and to
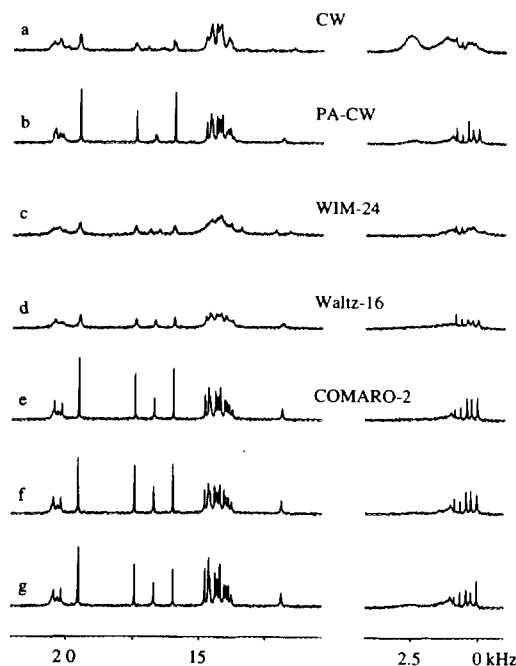

FIG. 6. $^{13}C\{^1H\}$ spectra of the liquid crystal I52 measured with different proton-decoupling schemes and a decoupler-field strength given by $\omega(^1H)/(2\pi) = 21$ kHz. The sharp peak with the lowest frequency was arbitrarily referenced to 0 Hz. (a) was measured with cw irradiation, and for spectrum (b) the phase of the irradiation was inverted every 300 μs. (c) employed WIM-24, (d) WALTZ-16, and (e) COMARO-2. Spectra (f) and (g) were measured with sequences [1] and [4], respectively.

the three methylene groups that are not part of a ring system or directly attached to a ring system. If this interpretation is correct, the signals that are only observed in the cw spectra represent the CH_2 groups with higher-order parameters. Since the CH fragments in the aromatic ring are expected to exhibit similarly large order parameters but appeared well decoupled, the poor performance of the multiple-pulse cycles in the aliphatic region is probably caused by large homonuclear dipolar couplings in the methylene groups. Further improvements of the sequences will have to address this problem. The MLEV-4 analogue constructed with the five-pulse inversion element (25) seemed to lose the least of the methylene signals and to resolve the aromatic resonances best (Fig. 6g). This sequence is the fastest to achieve homonuclear dipolar decoupling to zero-order approximation, and its length is about a factor of eight shorter than the COMARO-2 cycle.

CYCLES THAT RETAIN SCALED LINEAR INTERACTIONS

Homonuclear dipolar decoupling may be achieved while retaining scaled heteronuclear couplings and chemical-shift differences (14). The design of cycles with a finite scaling factor is a more demanding problem than the design of isotropic sequences, since the additional condition that the scaling of the linear interactions should be as small as possible has to be met. This implies, for instance, that the average of the pulse angles that are employed should be significantly smaller than 180°, which limits the range of useful composite pulses. Furthermore, the combination of cyclic pulse-train fragments with their 180° phase-shifted analogue inevitably reduces the average effective field to its z component. We tested some of the established sequences as well as new sequences of this kind which all consist of 90° pulses with orthogonal phases. For the static I52 sample our decoupling-field strength proved too low and we present only results obtained with the benzene sample. Our proton-detected local-field spectra of benzene oriented in a liquid crystal measured with the MREV-8 sequence displayed three doublets representing three different ^{13}C-^{1}H distances in the molecule (1). The coupling difference between the meta- and para-proton could not be resolved. On this basis one would expect the ^{13}C-detected separated local-field spectrum of the same sample to show a doublet × triplet × quartet. Experimentally we observed doublets × triplets with MREV-8 as well as BLEW-12, while the quartet structure was not clearly resolved (Figs. 7a and 7b). The results obtained with the BLEW-12 sequence varied significantly, depending on the spectrometer tune up. The spectra obtained with semiwindowless MREV-8 (6) were very sensitive to the pulse lengths, and the resolution was consistently low. With BR-24 (19), on the other hand, the signals were even broader, but here, the semiwindowless variant performed much better and the spectra displayed the quartet structure more reliably (Fig.
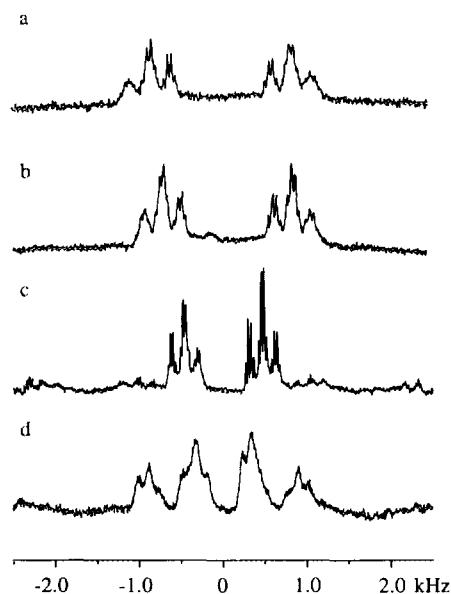

FIG. 7. $^{13}C\{^{1}H\}$ separated local-field spectra of the oriented benzene sample. The different proton-irradiation schemes used to acquire the spectra are MREV-8 (a), BLEW-12 (b), and semiwindowless BR-24 (c, d). Whereas the decoupler frequency was on resonance with the proton chemical-shift frequency for (a), (b), and (c), it was 1 kHz off resonance for (d). Assuming that the J couplings are not resolved and that the heteronuclear three- and four-bond couplings are too similar to be distinguished, the spectrum should display a doublet × triplet × quartet.

7c). However, much of the signal intensity is lost in sidebands of the main signal. Furthermore, upon moving the ^{1}H frequency 1 kHz off resonance, even the basic doublet pattern was lost (Fig. 7d). In contrast, the self-compensating BLEW-48 (6), which performed consistently well with the decoupler on resonance (Fig. 8a), sometimes achieved even better resolution when the decoupler frequency was moved off resonance (Fig. 8b). This may be understood in terms of "second averaging" (20). While the accuracy of the coupling constants obtained from such a spectrum will probably never approach that of a simulation of the fully coupled spectrum with resolved lines, these experiments could nevertheless provide good starting values in a short time.

Whereas BLEW-48 provided very good results, it is somewhat cumbersome to implement in 2D experiments mainly because of its low sampling rate and the number of pulses. Although one can oversample this cycle by a factor of 2, the time increment still includes twenty-four 90° pulses. (An oversampling by a factor of 4 is possible according to Ref. (6).) Searching for alternatives, we screened various non-cyclic propagators consisting of 90° pulses with orthogonal phases. Propagators with optimum scaling factors, such as the (1/3) propagator $y\bar{x}\bar{y}x$, did not work well, which is probably mainly due to violations of rule (B). It proved more successful to work with a less-favorable scaling factor. As an example, the spectrum produced by the (1/3) propagator with the pulse phases $\bar{y}x y\bar{y}$ is shown in Fig. 8c. It is

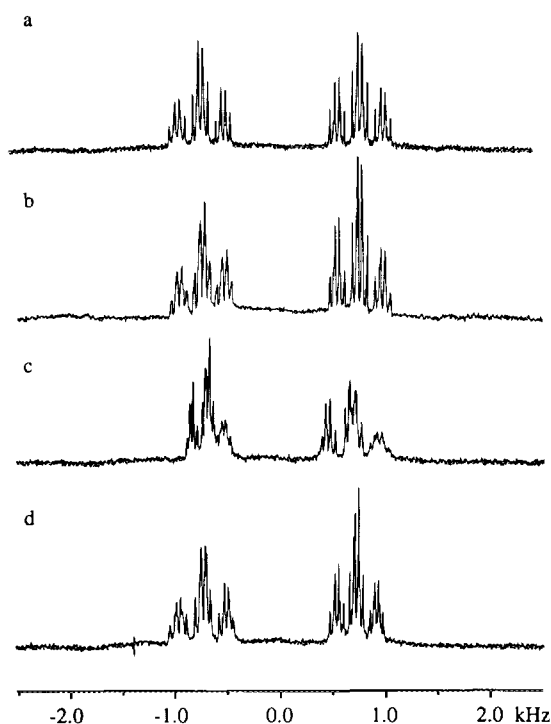FIG. 8. $^{13}C\{^1H\}$ separated local-field spectra of the benzene sample. Different proton-irradiation schemes were used to acquire the spectra. They include BLEW-48 with the decoupler frequency on resonance (a), BLEW-48 one kHz off resonance (b), and the four-pulse propagator $\bar{x}\bar{x}\bar{y}\bar{y}$ (c) and the six-pulse propagator $x\bar{y}\bar{x}\bar{x}\bar{y}\bar{x}$ (d), both 800 Hz off resonance.

at least as well resolved as the BLEW-12 spectra (Fig. 7b) but less symmetric—the asymmetry being often observed when using sequences that lack inversion symmetry. The experimental scaling factor was approximately 85% of that of BLEW-48, in good agreement with theoretical expectations (87%) based on the formula given in Ref. (6). There are many variations of these four pulses that keep the scaling factor unchanged, e.g., exchange of y and x pulse phases or inversions. However, none of these extended sequences showed much improved performance. It seems probable that although the actual effective field vector did not coincide with the theoretically expected vector, it was rather constant and identical to the intrinsic field of the basic propagator. The most promising noncyclic propagator was found to be the six-pulse inversion element that makes up the first part of BLEW-48 (phases $x\bar{y}\bar{x}\bar{x}\bar{y}\bar{x}$). The intrinsic scaling factor of this pulse group is exactly the same as that of the whole 48-pulse cycle, and we found its performance to be almost as good and consistently better than that of BLEW-12 (Fig. 8d). Since these six pulses represent a (1/2) propagator, the minimum dwell time includes twelve 90° pulses.

CONCLUSIONS

We screened ideas for the design of windowless multiple-pulse sequences and tested them in heteronuclear experi-

ments. Straightforward implementations of a recursive expansion scheme developed for heteronuclear decoupling in an isotropic liquid phase led to several isotropic sequences that compare favorably with the COMARO and WIM sequences in certain contexts. Noncyclic propagators with either vanishing or nonvanishing scaling factors were found to perform better than cyclic analogues with the same number of pulses. Our results seem to imply that high-resolution liquid-state probes can be used to obtain well-resolved ^1H-decoupled ^{13}C spectra of static liquid-crystalline samples. The main problem is large H,H couplings, e.g., geminal couplings in methylene groups with large order parameters.

ACKNOWLEDGMENTS

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