always be sufficiently larger for the better conjugated C_{2v} molecule than for the C_2 geometry to overcome the inherent preferences of the solute molecule. In order to minimize the effects of dispersion forces, we have included a neon matrix in our investigations, but even then, the results were the same.

Since it is difficult to imagine that a small deviation from planarity will affect the dispersion forces dramatically, we consider it very unlikely, although possible in principle, that an isolated molecule of the minor conformer of butadiene is nonplanar.

This conclusion disagrees with some of the best currently available calculations[3f] and agrees with others,[2c] but it must be emphasized that the calculated potential energy surface is very flat with respect to the $C_1C_2C_3C_4$ dihedral angle and thus to C_2–C_{2v} interconversion, so that the exact location of the minimum is undoubtedly extremely sensitive to the quality of the calculation. Since the correction for the electron correlation energy is most likely largest at the planar geometry, it is conceivable that calculations incorporating a larger fraction of the correlation effects will indeed produce a minimum at C_{2v} geometry. If improved calculations on an isolated molecule continue to predict a nonplanar geometry, it would be interesting to perform calculations for *s-cis*-butadiene surrounded by Ne atoms or perhaps already for the van der Waals complex of *s-cis*-butadiene with a single neon atom.

Conclusions

We have shown, employing the relatively simple technique of polarized matrix-isolation IR spectroscopy, that the minor rotamer of 1,3-butadiene is in fact planar within at most 10–15° in a wide variety of matrix environments and, hence, should be called *s-cis*-1,3-butadiene. Although we consider it very likely that this also is the geometry of this conformer in the gas phase, in disagreement with some of the best calculations available, this has not been strictly proven.

More generally, we have demonstrated the applicability of quantitative polarized IR spectroscopy to basic questions of molecular conformation, and this may stimulate further interest in this potentially important tool, applicable among others to molecules that cannot be readily observed except in matrix isolation.

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Registry No. 1,3-Butadiene, 106-99-0.

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^{17}O NMR Spectroscopy: Torsion Angle Relationships in Aryl Carboxylic Esters, Acids, and Amides

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Abstract: ^{17}O NMR spectroscopic data (natural abundance in acetonitrile at 75 °C) were obtained for the following series of electronically similar, sterically hindered compounds: aromatic methyl esters (**1–10**), aromatic carboxylic acids (**11–19**), and aromatic amides (**20–29**). Torsional angles were calculated by the molecular mechanics (MM2) method. Linear regression analysis of the estimated torsion angles and the ^{17}O chemical shift data for each series yielded the following results (series, slope δ/degree, correlation coefficient): esters (C=O), 0.70, 0.997; esters (–O–), 0.43, 0.992; acids ($-CO_2H$), 0.56, 0.994; amides (C=O), 0.84, 0.942; *N,N*-dimethylamides (C=O), 0.6, 0.991. The results are discussed in terms of minimization of repulsive van der Waals interactions by rotation of the functional group out of the plane of the aromatic ring.

^{17}O nuclear magnetic resonance spectroscopy is rapidly developing into a valuable method for examining a wide variety of structural problems[1] and may provide new insights into understanding chemical reactivity.[2] Carboxylic acids and their derivatives are among the most widely used synthetically and the most intensively studied of all functional groups. However, ^{17}O NMR studies of this important class of functional groups are limited to electronic effect studies in homologous series[3] or tabulations of chemical shift data on isolated types of compounds.[4] Recent findings have shown that ^{17}O NMR data for aromatic nitro compounds correlate well with torsion angles (X-ray).[5] In addition, ^{17}O NMR data for aryl ketones show a reasonable correlation with torsion angles (estimated by molecular mechanics calculations).[6] Determination of the solution-phase geometry of carbonyl-type functional groups has been under investigation for many years.[7] Classical methods used to estimate solution-

Table I. ^{17}O Chemical Shift Data (±1 ppm) for Aromatic Esters in CH_3CN at 75 °C

compd	Ar–CO_2Me	δ (C=O)	δ (–O–)	torsion angle,[a] deg
1	Ph	340	128	2
2	4-MeC_6H_4	339[b]	127[b]	2
3	2-MeC_6H_4	359	138.5	29
4	2,3-$Me_2C_6H_3$	363	141	29
5	2,6-$Me_2C_6H_3$	377	150	54
6	2,4,6-$Me_3C_6H_2$	376	149	54
7	1-naphthyl	361	139	33
8	2-naphthyl	341	129	2
9	9-anthryl	385	154	67
10	2,4,6-*t*-BuC_6H_2	392	162	76

[a] Calculated by molecular mechanics method (MM2) (±2°). See ref 15. [b] from ref 3; taken in acetone at 40 °C.

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Table II. ^{17}O Chemical Shift Data (±1 ppm) for Aromatic Carboxylic Acids in CH_3CN at 75 °C

compd	Ar–CO_2H	δ^a	torsion angle,^{b} deg
11	Ph	250.5	2
12	4-MeC_6H_4	249	2
13	2-MeC_6H_4	265	29
14	2,3-$Me_2C_6H_3$	269	29
15	2,6-$Me_2C_6H_3$	280	55
16	2,4,6-$Me_3C_6H_2$	280	55
17	1-naphthyl	267	35
18	2-naphthyl	251.5	2
19	9-anthryl	287	67

[a] Both oxygens. [b] Calculated by molecular mechanics method (MM2) (±2°). See ref 15.

Table III. ^{17}O NMR Chemical Shift Data (±1 ppm) for Aromatic Amides in CH_3CN at 75 °C

compd	Ar–$CONH_2$	δ(C=O)	torsion angle,^{a} deg
20	Ph	329	28
21	4-MeC_6H_4	327	28
22	2-MeC_6H_4	350	44
23	2,6-$Me_2C_6H_3$	353	60
24	1-naphthyl	359	51
25	2-naphthyl	331	27
26	9-anthryl	365	71
	Ar–$CONMe_2$		
27	Ph	348	62
28	1-naphthyl	352	71
29	9-anthryl	357	78

[a] Calculated by molecular mechanics method (MM2) (±2°); see ref 15.

phase torsion angles between aromatic rings and carbonyl-containing functional groups have included ultraviolet spectroscopy[7b,8,9] and dipole moment measurements,[9,10] and more recently ^{13}C NMR spectroscopy[11] has been employed. In this paper we report the ^{17}O NMR spectroscopic study of several series of electronically similar, sterically hindered compounds: aromatic methyl esters (**1–10**, Table I), aromatic carboxylic acids (**11–19**, Table II), and aromatic amides (**20–29**, Table III). Quantitative relationships between calculated (molecular mechanics) torsion angles and the ^{17}O chemical shift data have been obtained.

Results

Aromatic Methyl Esters. The ^{17}O chemical shift data for compounds **1–10**, listed in Table I are in the chemical shift region normally associated with esters. The ^{17}O chemical shifts of esters have been shown to be influenced by substituents attached to the carbonyl group[3,12] and to the single-bonded oxygen.[13,14] The ^{17}O chemical shifts of aromatic esters have been shown to be sensitive to electronic effects of substituents;[3,12] not surprisingly the double-bonded oxygen is approximately twice as sensitive to electronic effects as the single-bonded oxygen.[3] Variation of the size of the alkyl group attached to single-bonded oxygen significantly influences the chemical shift of the single-bonded oxygen, and although less pronounced, an easily detected effect is observed on the carbonyl oxygen resonance.[14] However, in this series (**1–10**), chemical shift differences resulting from electronic effects are small compared to those arising from steric influences and will be neglected.

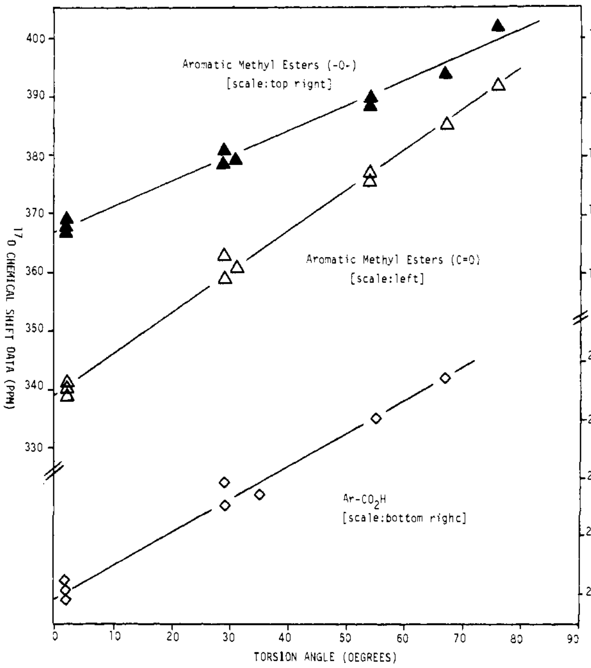

Figure 1. Plot of ^{17}O chemical shift data (ppm) for aromatic methyl esters and aromatic acids vs. calculated torsion angles of the functional group with the aromatic ring.

The signals for both the carbonyl oxygen and the single-bonded oxygen in the present results are both substantially deshielded in compounds which appear to have greater steric interactions. This result is consistent with rotation of the functional group from the plane of the aromatic ring. Such rotation would be expected to increase the double-bond character of both oxygen atoms which should result in deshielding of the oxygen signals. In view of our previous success in relating ^{17}O chemical shifts of ketones to calculated torsional angles,[6] we carried out molecular mechanics (MM2) calculations[15] on the aromatic esters. These calculations were carried out with the OCH_3 group in the *s-Z* conformation. The torsion angle estimations from the MM2 method are included in Table I and are defined as the difference angle between the plane of the carbonyl group and the plane of the aromatic ring. The calculated torsion angles for **1** and **6** (2° and 54°, respectively) are in reasonable agreement with the torsion angles deduced from dipole moment studies[10a] (0° and 47°). A plot of the calculated torsion angles vs. the chemical shift for both the double- and single-bonded oxygen is shown in Figure 1. Excellent correlations are obtained for both oxygen signals (vide infra).

Aromatic Carboxyic Acids. The ^{17}O chemical shifts for representative aliphatic[4] and aromatic carboxylic acids[3] have been reported and have been shown to be sensitive to electronic effects of substituents.[3] Table II contains the ^{17}O chemical shift values for a series of electronically similar aromatic carboxylic acids. As previously noted,[4] only one ^{17}O signal for the carboxylic acid functional group is detected. The equivalence of the two oxygens is attributed to fast proton exchange[4] in dimeric or higher aggregates. Qualitatively, it is apparent (Table II) that as steric hindrance to coplanarity of carboxylic function and the aromatic ring is increased, the magnitude of the carboxyl chemical shift increases; compare, for example, **11**, **17**, **15**, and **19**. The direction of the shift is consistent with the rotation of the functional group from the plane of the aromatic ring which will increase its overall double-bond character. Calculated torsion angles (MM2) for these

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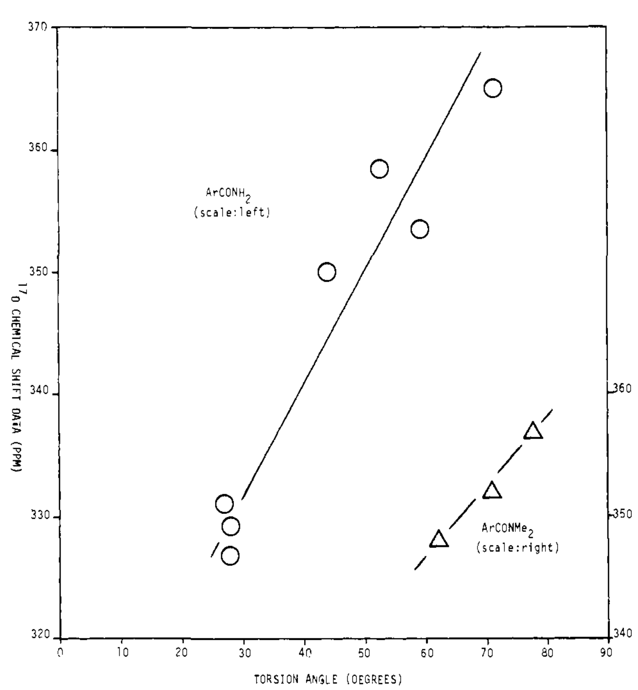

Figure 2. Plot of ^{17}O chemical shift data (ppm) for aromatic amides vs. calculated torsion angles of the amide functional group with the aromatic ring. The line shown for ArCONH$_2$ data assumes a linear relationship (see text).

compounds are also included in Table II. An excellent correlation between estimated torsion angle and ^{17}O chemical shift can be noted in Figure 1. Torsion angle data appear in the literature for two compounds included in this study. For example, the torsion angle estimated here for **15** (55°) is in good agreement with the X-ray value[16] (51.5°) and the value (50.7) estimated by ^{13}C NMR methods.[11a] However, the calculated value for **14** (29°) does not agree with X-ray data[16] (10°) but is reasonably consistent with the value obtained from the ^{13}C NMR approach (25°).[11a] For **14**, it is likely that the conformation in solution is different from that of the crystalline material.

Aromatic Amides. Table III contains the ^{17}O chemical shift values, as well as the calculated torsion angles, for electronically similar, hindered aromatic amides. The ^{17}O chemical shifts for representative simple amides have been reported;[17-19] however, the most extensive examination of amide chemical shifts has occurred in the peptide field.[20] The chemical shifts of amides have been shown to be dependent upon conformation and hydrogen bonding.[17,20,21] The chemical shift of this functional group has been demonstrated to have contributions from the amide function acting as both a hydrogen bond donor and an acceptor.[20]

It is apparent from the data that the chemical shift range is compressed compared to that of the ester carbonyl data reported here. This compression is due, in part, to the fact that for the least hindered compound, benzamide, the amide-aromatic ring torsion angle is not near zero, as in the case of methyl benzoate, but is 26° as determined by X-ray analysis.[22] The molecular mechanics calculated torsion angle (28°) is in good agreement with the X-ray data. The quality of the correlation for the simple amides, apparent from Figure 2, is not as good as that obtained with the other two series of compounds. Although a linear relationship is shown in Figure 2, the data for the simple amides (ArCONH$_2$) appear to exhibit scatter or curvature. This may reflect complications arising from hydrogen-bonding interactions.

Table IV. Linear Regression Correlations of ^{17}O Chemical Shift Data with Calculated Torsion Angles (MM2)

series	slope (δ/angle, deg)^a	r^b	intercept	n^c
ester (C=O)	0.70 ± 0.04^a	0.997	339 ± 2	10
ester (-O-)	0.43 ± 0.03	0.992	127 ± 2	10
acid	0.56 ± 0.05	0.994	249 ± 2	9
amides (C=O)	0.84 ± 0.5	0.942	308 ± 16	7
N,N-dimethylamides (C=O)	0.6^d	0.991	313^d	3
ketones (C=O)^e	0.84 ± 0.14^e	0.979	553 ± 6	10
nitro compounds (NO$_2$)^f	0.76 ± 0.14^f	0.987	574 ± 16	7

^{a}Error limits shown are 95% confidence limits. ^{b}Correlation coefficient. ^{c}Number of data points. ^{d}Limited number of data points. ^{e}Recalculation of data of ref 6. ^{f}Recalculation of data of ref 5.

In order to eliminate possible complications arising from hydrogen bonding, a limited number of *N,N*-dimethylcarboxamides (Table III) were examined. However, the added steric interactions arising from the *N,N*-dimethyl group add substantially to the torsion angle in this system as noted in Table III. For example, the predicted (MM2) torsion angle for *N,N*-dimethylbenzamide is 62°. Because of this additional steric hindrance, the range of torsion angles is limited and the chemical shift range is correspondingly reduced. Despite the limited number of compounds studied, it is clear that the slope of the correlation for the *N,N*-dimethylamides is reduced from that of the simple amides.

Torsion Angle Relationships. Linear regression analysis of the calculated torsion angles (MM2) and ^{17}O chemical shift data for each series of carbonyl compounds is listed in Table IV. All data for the esters and acids give excellent correlations. The slope for the data of the single-bonded ester oxygen (0.43 δ/angle (deg)) is approximately one-half that of the slope for the carbonyl oxygen (0.70 δ/angle) (deg)); their average value (0.56 δ/angle (deg)) is the value noted for the carboxylic acids (see Table IV). These results are consistent with the correlations observed for substituent effect studies on benzoic acids and esters.[3] The correlation for simple amides is poor. The origin of the poor correlation is not clear; it may be attributable to variations in the ^{17}O results arising from differences in hydrogen bonding and/or it may reflect slight changes in the partial pyramidal structure of the amide nitrogen.[23] The slope (0.6 δ/angle (deg)) for the *N,N*-dimethylamides is consistent with expectations and may reflect the absence of H-bonding problems (despite the limited number of data points). The slope for the amides would be expected to be somewhat less than that for the ester carbonyl on the basis of resonance considerations. For the sake of comparison the correlations for aromatic ketones[6] and nitro compounds[5] have been recast in the present format and show that torsion angle effects in all the series are of similar magnitude.

Discussion

Compressional effects on ^{17}O chemical shifts have been noted in several systems. The effects of steric interactions on single-bonded oxygens in both conformationally mobile and locked systems have been carefully examined.[24] A limited number[25] of examples of steric effects on carbonyl groups have been reported, including recognition of a deshielding delta (δ) effect.[26] Isolated examples of the effect of torsion angle rotation for carbonyl groups on their ^{17}O chemical shift have been noted.[27] Recent work[2] on

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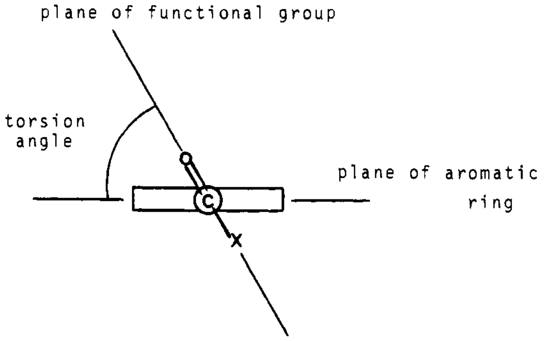

Figure 3. Perspective views which illustrate the torsion angle between the planes of the aromatic ring and the functional group.

planar carbonyl systems has shown major deshielding shifts arising from substantial steric interactions. These latter results were explained in terms of the direct effect of repulsive van der Waals interactions on the ^{17}O chemical shift of the carbonyl group. This suggestion is consistent with the recent report of correlations between local van der Waals steric energy and the chemical shift of the resonant nuclei for several classes of compounds.[28] It was suggested[28] that repulsive van der Waals interactions cause contraction of orbitals of the resonant nuclei, thus leading to an increase in r^{-3} of the paramagnetic term (Karplus–Pople equation[29]) and resulting in a deshielding effect. In the systems reported here repulsive van der Waals interactions are readily minimized by rotation of the functional group out of conjugation with the aromatic ring (see Figure 3). Thus the correlation of ^{17}O chemical shift with torsion angle is an indirect consequence of the minimization of van der Waals interactions. This represents a distinctly different origin of deshielding effects for ^{17}O chemical shifts stemming from van der Waals interactions in sterically hindered rigid molecules.[2]

Since the electronic effects of substituents in the systems studied here are minimal, the slopes in Table IV are intrinsic for the various conjugated functional groups in acyclic systems. Therefore, this approach should be useful for making torsion angle estimations in sterically hindered systems having substituents which also exert substantial electronic effects. Such estimations can be achieved by correcting for the contribution to the chemical shift value for the electronic term. The resulting chemical shift difference can be used in conjunction with the appropriate slope from Table IV to predict the average torsion angle for the hindered molecule. In contrast to the ^{13}C NMR method for estimation of torsion angles, this approach provides a direct observation of the functional group and is applicable to a wide range of conjugated oxygen-containing systems. This approach should be generally applicable and should allow the estimation of torsion angles for oxygen-containing conjugated functional groups by a direct method.

Experimental Section

Those compounds used in this study that were not commercially available were prepared and purified by standard literature procedures. They were characterized by spectroscopic (^{1}H and ^{13}C NMR spectroscopy) and physical data. The ^{17}O spectra were recorded on a JEOL GX-270 spectrometer equipped with a 10-mm broad-band probe operated at 36.5 MHz. All spectra were acquired at natural abundance at 75 °C in dried acetonitrile containing 1% of 2-butanone or acetone as an internal standard. The concentration of the carbonyl compounds employed in these experiments was 0.5 M. The signals were referenced to external deionized water at 75 °C. The 2-butanone resonance (558 ± 1 ppm) or acetone (571 ± 1 ppm) was used as an internal check on the chemical shift measurements for these compounds. The instrumental settings were spectral width 25 kHz, 2K data points, 90° pulse angle (28 μs pulse width), 200 μs acquisition delay, 40 ms acquisition time, and 40000–100000 scans. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a 25-Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to ±0.2 ppm by zero filling to 8K data points. The reproducibility of the chemical shift data is estimated to be ±1.0. Molecular mechanics calculations were carried out by use of the MM2 program model version 1.3, available from Professor C. Still, Columbia University.

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Registry No. 1, 93-58-3; **2**, 99-75-2; **3**, 89-71-4; **4**, 15012-36-9; **5**, 14920-81-1; **6**, 2282-84-0; **7**, 2459-24-7; **8**, 2459-25-8; **9**, 1504-39-8; **10**, 57198-99-9; **11**, 65-85-0; **12**, 99-94-5; **13**, 118-90-1; **14**, 603-79-2; **15**, 632-46-2; **16**, 480-63-7; **17**, 86-55-5; **18**, 93-09-4; **19**, 723-62-6; **20**, 55-21-0; **21**, 619-55-6; **22**, 527-85-5; **23**, 55321-98-7; **24**, 2243-81-4; **25**, 2243-82-5; **26**, 34810-13-4; **27**, 611-74-5; **28**, 3815-24-5; **29**, 38308-87-1.

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