

acid and then saturated aqueous sodium bicarbonate solution. The ether layer was washed with water, dried (MgSO_4), and concentrated under reduced pressure. The residue was the practically pure tosylate (17.2 g). The ir spectrum (neat) did not show the absorption of OH stretching but the characteristic absorption of a tosylate: 1363 and 1177 cm^{-1} . The *exo-3.3.0-7-en-2-yl* tosylate was prepared by a similar procedure, ir 1360 and 1170 cm^{-1} .

exo-cis-Bicyclo[3.3.0]oct-7-en-2-yl Acetate.—A mixture of 10.5 g of the *endo-3.3.0-7-en-2-yl* tosylate, 11.3 g of tetraethylammonium acetate, and 250 ml of acetone was refluxed for 22 hr. After evaporation of acetone, the residue was poured into 400 ml of water. Then the mixture was extracted five times with 200 ml portion of ether. The ether extracts were combined, washed with water, dried (Na_2SO_4), and concentrated. Distillation afforded 6.7 g of the *exo-3.3.0-7-en-2-yl* acetate: bp 69–73° (5 mm); ir, 1730, 1020, and 720 cm^{-1} , mass spectrum m/e 106 ($\text{M}^+ - \text{CH}_3\text{CO}_2\text{H}$) (the molecular peak, 166, was not observed).

exo-cis-Bicyclo[3.3.0]oct-7-en-2-ol.—A mixture of 6.7 g of the *exo-3.3.0-7-en-2-yl* acetate, 2 g of sodium hydroxide, 2 drops of water, and 20 ml of methanol was refluxed for 10 hr. On cooling, the mixture was neutralized with concentrated hydrochloric acid. The precipitated sodium chloride was filtered off and the filtrate was concentrated. Distillation gave 3.8 g of the *exo-3.3.0-7-en-2-ol*: bp 79–83° (5 mm) [lit.¹² bp 71–72° (3 mm)]; ir (neat) 3360 cm^{-1} .

endo-cis-Bicyclo[3.3.0]oct-7-en-2-yl Acetate.—A solution of 0.5 g of the *endo-3.3.0-7-en-2-ol* in 0.85 g of acetic anhydride was fluxed for 6 hr. The mixture was poured into 50 ml of saturated aqueous sodium bicarbonate solution and extracted with five 50-ml portions of ether. The ether extracts were combined,

washed with water, dried (Na_2SO_4), and concentrated. Distillation afforded 0.6 g of the *endo-3.3.0-7-en-2-yl* acetate: bp 69–73° (6 mm); ir (neat) 1723, 790, and 765 cm^{-1} , mass spectrum m/e 106 ($\text{M}^+ - \text{CH}_3\text{CO}_2\text{H}$) (the molecular peak, 166, was not observed).

exo- and endo-cis-Bicyclo[3.3.0]oct-7-en-2-yl Trifluoroacetates.—Each trifluoroacetate was prepared from trifluoroacetic anhydride (1.5 ml) and the corresponding alcohol (0.2 g) by the similar procedure described above. The dried ether extract was concentrated under reduced pressure and used for nmr measurement without isolation. The ir spectrum of the nmr sample showed the absence of hydroxyl group and the presence of carbonyl group of trifluoroacetate: the *exo* isomer, 1775 cm^{-1} ; the *endo* isomer, 1779 cm^{-1} .

exo- and endo-cis-Bicyclo[3.3.0]oct-7-en-2-yl Formates.—A mixture of 0.2 g of the corresponding alcohol, 3 ml of formic acid, and 0.2 g of anhydrous sodium sulfate was heated at 80° for 4 hr. Then the mixture was poured into 150 ml of saturated aqueous sodium bicarbonate solution, extracted with four 50-ml portions of ether. The ether layer was washed with water, dried (Na_2SO_4), and concentrated. Distillation of the formate afforded the *exo-3.3.0-7-en-2-yl* formate, bp 84–86° (20 mm), ir (neat) 1718 cm^{-1} , mass spectrum m/e 106 ($\text{M}^+ - \text{HCO}_2\text{H}$) (the molecular peak, 152, was not observed), and the *endo-3.3.0-7-en-2-yl* formate, bp 73–74° (12 mm), n_D^{20} 1.4852, ir (neat) 1716 cm^{-1} , mass spectrum m/e (rel intensity) 152 (1.59, M^+), 106 (100, $\text{M}^+ - \text{HCO}_2\text{H}$).

endo-cis-Bicyclo[3.3.0]oct-7-en-2-yl Chloroformate.—Dry phosgene gas was bubbled into a solution of 0.1 g of the *endo-3.3.0-7-en-2-ol* in 1 ml of carbon tetrachloride during 20 min at 15°. The solution was kept standing for 30 min at room temperature. Then dry nitrogen was bubbled for 15 min in order to purge excess phosgene and hydrogen chloride formed. The mixture was used for nmr measurement without isolation.

(12) N. A. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964).

Nuclear Magnetic Resonance Spectroscopy.

The Carbon-13 Spectra of Some Cyclic Alkynes, Allenes, and Alkenes¹

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The ¹³C nuclear magnetic resonance (nmr) spectra of selected examples of cyclic alkynes, allenenes, and alkenes are reported and discussed. The possible effects of diamagnetic anisotropy on the differences of carbon chemical shifts between cyclic and acyclic alkynes are considered. Other possible sources of carbon chemical-shift differences in these compounds are discussed.

The chemical shifts of sp-hybridized carbons have been of interest to nuclear magnetic resonance (nmr) spectroscopists for several years.^{2–5} More recently, technological advances in the maintenance of stable magnetic fields and proton decoupling have made possible the resolution of the carbon resonances of the entire alkyne molecule, so that the substituent effects of the alkyne moiety on the chemical shift of neighboring carbons could be studied.^{6,7} It was evident from these last studies that the triple bond appears to have a larger effect upon carbon than proton chemical shifts. The

present study seeks to extend our knowledge of the effect of diamagnetic anisotropy in carbon chemical shifts, and to investigate the differences in the responses of protons and carbons to neighboring multiple bonds.

Experimental Section

The compounds used in this study were obtained from commercial sources or were prepared by known literature procedures. Data for the compounds are presented in Table I.

Carbon-13 chemical shifts were measured under conditions of full proton decoupling on a Varian digital frequency sweep spectrometer described previously.⁸ Spectra were obtained in benzene solution. Chemical shifts were measured relative to internal cyclohexane (ca. 5%) and later referenced to external carbon disulfide by the relation $\delta_{\text{CS}_2} = \delta_{\text{C}_6\text{H}_{12}} + 166.2$ ppm.

Results

The carbon-13 chemical shifts are summarized in Table II. The assignments of resonances were based

(1) Supported by the National Science Foundation, and by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences.

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(7) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

(8) (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967); (b) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S. A.*, **60**, 1152 (1968).

TABLE I
PREPARATIONS AND PHYSICAL PROPERTIES

Compd	Mp or bp, °C (mm)	Ref
1,7-Octadiyne	93-95 (190)	a
4,6-Decadiyne	i	
Cyclotridecyne	84-86 (3)	b
Tetradeca-1,7,13-triyne	i	
Cyclotetradeca-1,8-diyne	i	
Tetradeca-1,6,8,13-tetrayne		c
Cyclotetradeca-1,3,8,10-tetrayne	115-120 dec	c
Hexadeca-1,7,9,15-tetrayne	15-17	d
Cyclohexadeca-1,3,9,11-tetrayne	160-162 dec	d
Octadeca-1,8,10,17-tetrayne		c, e
Cyclooctadeca-1,3,10,12-tetrayne	210-212	c, e
Cycloheptacos-1,3,10,12,19,21-hexayne	125	c, e
Cyclohexatriaconta-1,3,10,12,19,21,28,30-octayne	135	c, e
Cyclohexa-1,4-diene	i	
Cycloocta-1,5-diene	i	
cis,cis-Cyclotetradeca-1,8-diene	43	f
Cyclonona-1,2-diene	62-63 (16)	g
Cyclonona-1,2,6-triene	61-62 (13)	g
Cyclodeca-1,2,6,7-tetraene	48-50 (0.7)	g
Cyclotrideca-1,2-diene	90 (5)	b, g, h
Cyclohexadeca-1,2,9,10-tetraene	80	g

^a H. Bader, L. C. Cross, I. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 619 (1949). ^b H. Nozaki, S. Kato, and R. Noyori, *Can. J. Chem.*, **44**, 1021 (1966). ^c F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Amer. Chem. Soc.*, **79**, 6263 (1957). ^d F. Sondheimer and Y. Amiel, *ibid.*, **79**, 5817 (1957). ^e F. Sondheimer, Y. Amiel, and R. Wolovsky, *ibid.*, **81**, 4600 (1959). ^f D. J. Cram and N. L. Allinger, *ibid.*, **78**, 2518 (1956). ^g L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963). ^h H. Nozaki, T. Aratane, and R. Noyori, *Tetrahedron*, **23**, 3645 (1967). ⁱ Product commercially available from Farchan and used without prior purification or analysis.

upon the following criteria: (1) molecular symmetry which, in many cases, gives rise to differing peak heights; (2) coherent proton decoupling frequencies for the various carbon resonances which could be compared with the partially resolved proton nmr spectra; (3) nuclear Overhauser enhancements which were expected to be attenuated in cases of carbons which have no proximal protons.⁹ The last criterion is useful in assignment of the resonances of conjugated diyne systems, in which the resonances of the inner pair of carbons are of smaller peak height than those of this outer pair. It should be noted that this assignment of these resonances is in accord with the finding that carbons which are α to a triple bond are shielded by some 10-15 ppm.^{6,7} Thus, in conjugated diyne systems, the inner pair of carbons is shielded by adjacency of the other triple bond, while the outer carbons are not.

In many cases, the above criteria were not sufficient and many of the resonances within a spectrum could not be surely assigned. Such instances are denoted by asterisks in Table II. This problem becomes particularly acute when the ring contains only one functional group (*cf.* cyclotridecyne), and has prevented the assessment of substituent effects of unsaturated groups in medium and large rings.^{10,11}

(9) A. J. Jones, D. M. Grant, and K. F. Kuhlman, *J. Amer. Chem. Soc.*, **91**, 5013 (1969).

(10) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 1347 (1970).

(11) J. Graefe, K. Herwig, D. E. Dorman, and J. D. Roberts, in preparation.

Discussion

The Cycloalkynes.—The simplest cycloalkyne examined in this study is cyclotridecyne (**3**). It is interesting to note that any strain in the triple-bonded carbons resulting from the cyclic nature of **3** appears to have a negligible effect on the chemical shift of the sp³-hybridized carbons. Thus, the unsaturated carbons of **3** come into resonance at 112.4 ppm,¹² while carbons 7 and 8 of tetradeca-1,7,13-triyne (**4**), the closest acyclic model in this study, resonate at 112.7 ppm.¹³ This conclusion is in accord with other studies of the cmr spectra of cis and trans cycloalkenes,¹¹ in which differences in ring strain were found to have only small effects upon the chemical shifts of the unsaturated carbons.

Except for the α carbons (C-3, -13), the effect of the triple bond on the chemical shifts of the saturated carbons of **3** is difficult to assess because of problems in assigning the resonances to particular carbons. The α carbons are shifted strongly upfield, occurring at almost 10 ppm higher field than the remaining sp³-hybridized carbons. Again, this is in general accord with previous results.^{6,7} The resonance of carbon 8, which, in principle, is identifiable because of the molecular symmetry, apparently falls beneath the overlapping resonances at 167.3 ppm. The remaining resonances range over about 2 ppm and are centered at about 166 ppm. The chemical shift of the single resonance of cyclotridecane is reported to be approximately 167 ppm.¹⁴ The spectra of *cis*- and *trans*-cyclotridecene¹¹ show a spread similar to that for **3**, although the spectrum of **3** compares most closely to that of the *trans* example. In the absence of specific assignments, however, the origins of these chemical-shift differences cannot be dissected further.

Better success is possible in comparisons of the spectra of compounds **5-11**, for which the principles discussed in the Results section of this paper suffice to give complete assignments. The spectra of closely related cyclic and acyclic polyynes are compared in Table III. For the pair A, there are some very large and obvious differences. Thus, the sp³-hybridized carbons (**7**) are deshielded by approximately 2.5 ppm relative to the analogous carbons of the conjugated diyne moiety of **6**. From what was said earlier, these differences seem larger than would be the case for ring-strain effects. Furthermore, there are changes of comparable magnitude in the chemical shifts of the sp³-hybridized carbons. Because of the possible importance of the diamagnetic anisotropy of the triple bond,^{6,15} it seems appropriate to see if these chemical-shift changes can be attributed to this phenomenon.

Diamagnetic anisotropy associated with the triple bond arises from interactions between the magnetic

(12) All chemical shifts in this paper are related to external carbon disulfide, with positive numbers representing upfield shifts. The chemical shift of external carbon disulfide on the TMS scale is approximately -193.7 ppm: G. C. Levy and J. D. Cargioli, *J. Magn. Resonance*, **6**, 143 (1972).

(13) It will be noted that the chemical shifts of the cycloalkynes reported in this paper differ in some regards from those reported previously.⁷ These disparities are probably due to the different solvents used in the two studies. A deshielding solvent effect has already been noted for benzene: J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).

(14) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964).

(15) (a) H. M. McConnell, *J. Phys. Chem.*, **27**, 226 (1956). (b) A number of modifications of the McConnell procedure have also been suggested; *cf.* J. A. Pople, *J. Amer. Chem. Soc.*, **88**, 4811 (1966), R. S. Macomber, *J. Org. Chem.*, **37**, 1205 (1972), and J. W. ApSimon, *Tetrahedron*, **23**, 2339 (1967).

TABLE II
CARBON CHEMICAL SHIFTS^a IN SELECTED ALKYNES, CYCLOALKYNES, CYCLOALLENES, AND CYCLOALKENES

Compd	1	2	3	4	5	6	7	8	9	10
1,7-Octadiyne (1)	124.0	109.2	175.3	165.6						
4,6-Decadiyne (2)	180.1	171.1	172.2	117.0	127.3					
Cyclotridecyne (3)	112.4	112.4	174.4	165.5*	166.6*	167.1*	167.3*	167.3*		
Tetradeca-1,7,13-triyne (4)	124.6	109.6	175.2	165.1*	165.5*	174.9	112.7			
Cyclotetradeca-1,8-diyne (5)	112.7	112.7	174.6	165.0	166.3					
Tetradeca-1,6,8,13-tetrayne (6)	124.0	110.4	175.8	165.9	175.1	116.9	126.7			
Cyclotetradeca-1,3,8,10-tetrayne (7)	114.5	123.8	123.8	114.5	173.3	168.9				
Hexadeca-1,7,9,15-tetrayne (8)	124.5	109.7	175.4	165.7*	165.7*	174.6	116.5	127.1		
Cyclohexadeca-1,3,9,11-tetrayne (9)	115.4	126.0	126.0	115.4	173.9	166.3				
Octadeca-1,8,10,17-tetrayne (10)	124.7	109.3	175.1	165.3*	165.3*	165.3*	174.3	116.4	126.9	
Cyclooctadeca-1,3,10,12-tetrayne (11)	116.7	125.8	174.3	165.9	166.5					
Cycloheptacos-1,3,10,12,19,21-hexayne (12)	116.0	126.4	174.2	165.5	165.8					
Cyclohexatriaconta-1,3,10,12,19,21,28,30-octayne (13)	116.0	126.6	174.3	165.4	165.4					
Cyclohexa-1,4-diene (14)	69.0	69.0	167.4							
Cycloocta-1,5-diene (15)	64.8	64.8	165.1							
<i>cis,cis</i> -Cyclotetradeca-1,8-diene (16)	63.3	63.3	166.8	165.0*	165.6*					
Cyclonona-1,2-diene (17)	101.0	-12.8	101.0	165.8	167.7*	165.1*				
Cyclonona-1,2,6-triene (18)	103.2	-13.0	103.2	166.3*	164.6*	63.3				
Cyclodeca-1,2,6,7-tetraene (19)	103.5	-14.6	103.5	166.9						
Cyclotrideca-1,2-diene (20)	101.9	-11.5	101.9	165.7	166.0*	166.0*	166.4*	166.6*		
Cyclohexadeca-1,2,9,10-tetraene (21)	103.1	-12.0	103.1	163.9	164.8	165.9				

^a In parts per million, relative to external carbon disulfide.¹² The figures for chemical shifts marked with asterisks represent uncertain assignments.

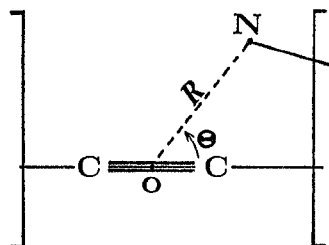


Figure 1.—A definition of the parameters of the McConnell equation.¹⁵ The brackets represent the remainder of the molecule in generalized form. O is the electrical center of gravity of the triple bond; R is the distance between O and the nucleus N, which is also in the same molecule; and θ is the angle between the symmetry axis of the triple bond and the ray R.

field (H_0) and the motion of the π electrons of the triple bond. An induced magnetic field results, the character of which, in the simplest case, may be approximated by point dipole at O (Figure 1).^{15a} If N is a nucleus in the same molecule, it experiences the small field of this point dipole and the effective magnetic field at N is thereby altered. The strength of the field of the point dipole is dependent on the angle between the applied external magnetic field and the symmetry axis of the triple bond, but in liquids rapid molecular tumbling average this last effect so that the effective field at N is dependent only on R, θ , and a constant which represents the anisotropy of the triple bond, $\Delta\chi$. The dependence of σ_g , the screening of N owing to the anisotropy of the triple bond, is given by the following relation.^{15a}

$$\sigma_g = \frac{\Delta\chi}{3R^3} (1 - 3 \cos^2 \theta) \quad (1)$$

A polar plot of $(1 - 3 \cos^2 \theta)/R^3$ (Figure 2) shows that, for θ angles of less than approximately 54.7° , σ_g is positive and the nucleus N is shielded. For larger angles, however, the effect of the triple bond will be deshielding in character. The single point dipole

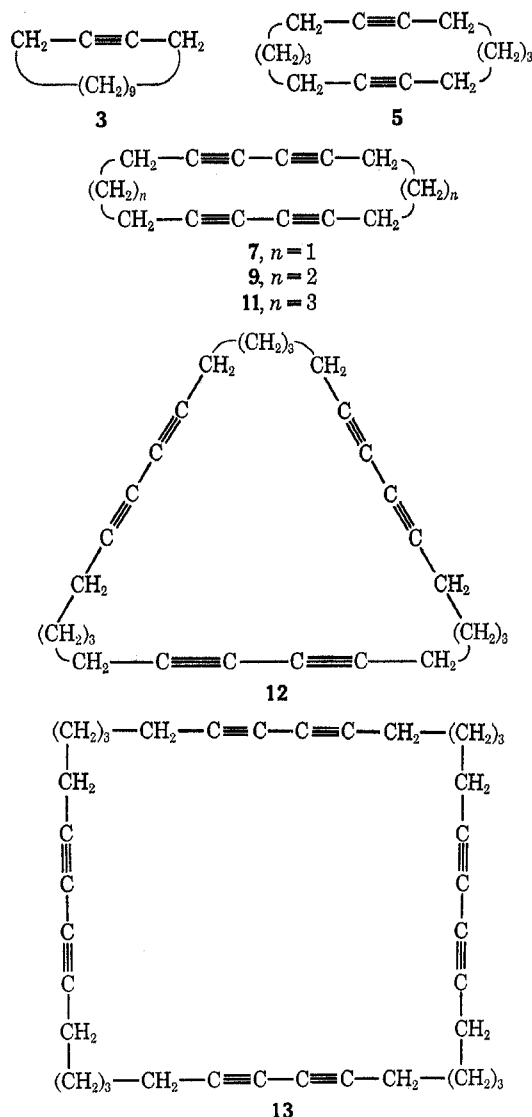


TABLE III
COMPARISON OF CARBON CHEMICAL SHIFTS IN SOME CLOSELY RELATED CYCLIC AND ACYCLIC POLYNYNES^a

		$-\text{CH}_2\text{CH}_2\text{C}\equiv\overset{\alpha}{\text{C}}\overset{\beta}{\text{C}}\overset{\gamma}{\text{C}}\overset{\delta}{\text{C}}\text{CH}_2\text{CH}_2-$				
Compd		α	β	γ	δ	ϵ
A	Cyclotetradeca-1,3,8,10-tetrayne (7)	-2.9	-2.4	-1.9	+2.0	
	Tetradeca-1,6,8,13-tetrayne (6)					
B	Cyclohexadeca-1,3,9,11-tetrayne (9)	-1.1	-1.1	-0.7	+0.6	
	Hexadeca-1,7,9,15-tetrayne (8)					
C	Cyclooctadeca-1,3,10,12-tetrayne (11)	-1.1	+0.3	0.0	+0.5	+1.2
	Octadeca-1,8,10,17-tetrayne (10)					
D	Cycloheptacos-1,3,10,12,19,21-hexayne (12)	-0.5	-0.4	-0.1	+0.2	+0.5
	Octadeca-1,8,10,17-tetrayne (10)					
E	Cyclohexatriaconta-1,3,10,12,19,21,28,30-octayne (13)	-0.3	-0.4	0.0	+0.1	+0.1
	Octadeca-1,8,10,17-tetrayne (10)					
F	Cyclotetradeca-1,8-diyne (5)	0.0	0.0	-0.3	-0.1	
	Tetradeca-1,7,13-triyne (3)					

^a Pairs of compared compounds are enclosed in brackets. The tabulated shift differences were obtained by subtracting the cmr spectrum of the second member of the pair from that of the first.

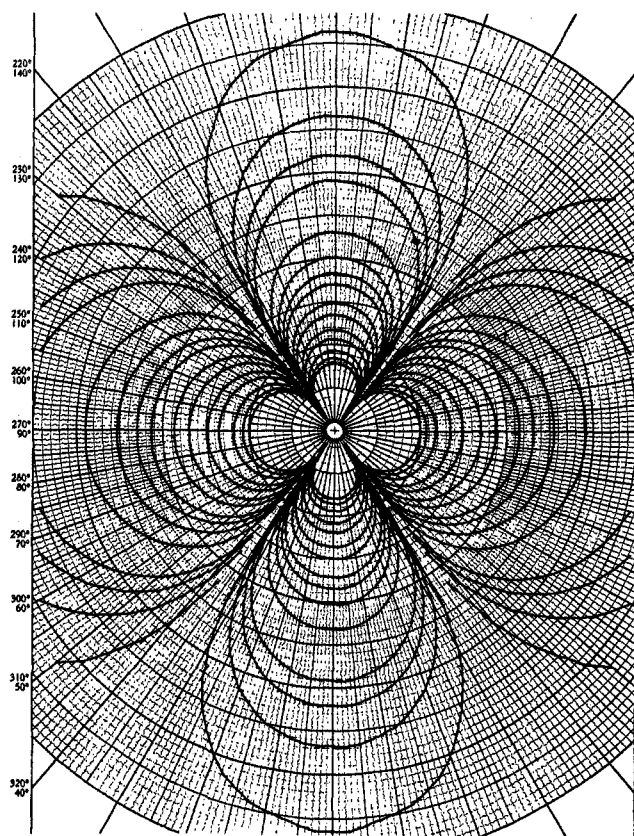


Figure 2.—Polar plot of constant values of $(1 - 3 \cos^2 \theta)/R^3$, where θ is 0° or 180° when R lies along the bond axis and R is the distance from the center of the bond. The contours from the inside out are at 1.0, 0.8, 0.6, 0.4, 0.3, 0.2, 0.15, 0.1, 0.08, 0.06, 0.04, 0.02, 0.015, 0.01, 0.005. The contours are negative for the horizontal lobes and positive for the vertical lobes. The bond axis is in the horizontal direction. The outer-most circle is 10 Å from the bond center. The figures printed along the side are values of $\theta - 90^\circ$ or $\theta + 90^\circ$. In using these plots it is very convenient to sketch the pattern of the molecule on a transparent overlay which can be positioned so as to easily see where particular atoms fall in the shielding or deshielding zones.

approximation has obvious shortcomings for calculating magnetic shielding produced by triple bonds in that it does not well reflect the over-all electron distributions of such bonds. Better results would be expected from Pople's procedure,^{15b} where the shielding could be simulated by two point dipoles (1,2) centered on each end

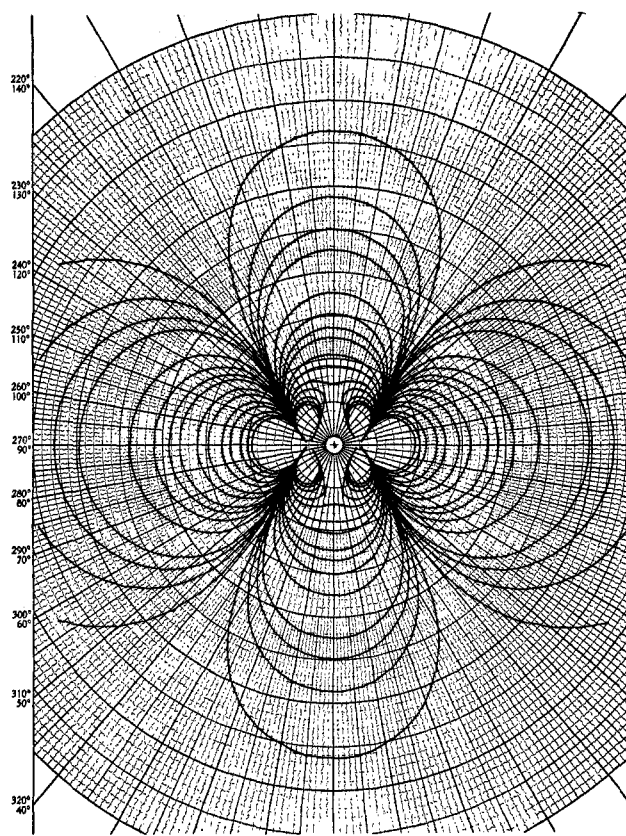


Figure 3.—Polar plot of constant values of $(1 - 3 \cos^2 \theta_1)R_1^2 + (1 - 3 \cos^2 \theta_2)/R_2^3$, where the distance between the point dipoles is 1.20 Å. The other features are as in Figure 1.

of the bond (1.20 Å apart). A polar plot of $(1 - 3 \cos^2 \theta_1)/R_1^3 + (1 - \cos^2 \theta_2)/R_2^3$ is shown in Figure 3. The important conclusions that can be derived from a comparison of Figures 2 and 3 are (1) that the shielding and deshielding regions have roughly similar angular dependences once one gets about 1.5 Å away from the center of the double bond, and (2) that the shielding and deshielding effects are predicted to fall off rather faster with distance from the bond center for the split dipole model. This means that the calculated shielding (or deshielding) effects will be generally smaller for the split dipole model, other things being the same.

Calculation of magnetic anisotropy effects with many of the substances considered here is complicated

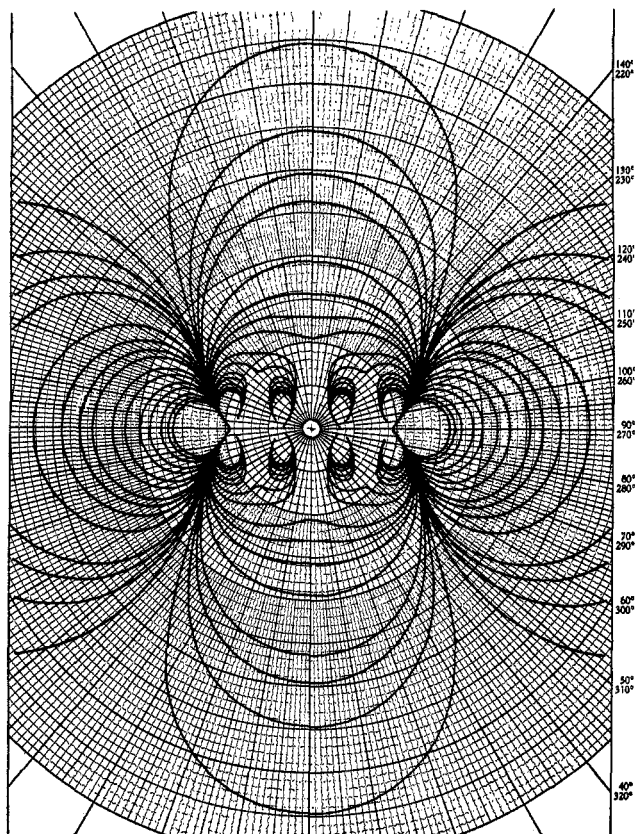


Figure 4.—Polar plot of constant values of $\Sigma(1 - 3 \cos^2 \theta_1)/R_1^3$ for four split dipoles corresponding to two triple bonds, each 1.20 Å in length and separated by 1.38 Å. The other features are as in Figure 2.

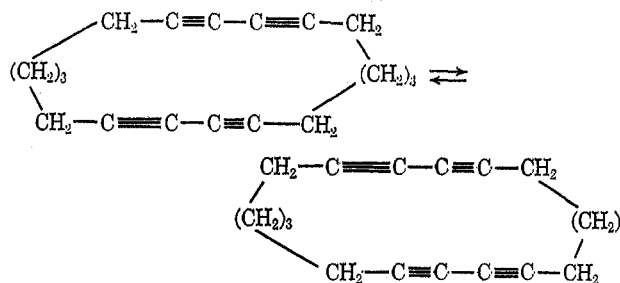
by the fact that it is not clear how the shielding and deshielding volumes will be changed by conjugation of triple bonds. We will assume here that two conjugated triple bonds can be approximated by assuming that there are two point dipoles, one at the center of each of the triple bonds, or else by four point dipoles centered on each carbon. The former case is represented by Figure 3, if it is rescaled so that the distance between the dipoles is about 2.6 Å instead of 1.2 Å and considered to be for two bonds, not one. The latter case with four point dipoles is shown in Figure 4, on the assumption that all of the dipoles are equivalent. With either of these approximations it is clear that carbons marked α and β (see Table III) should be deshielded by the pair of triple bonds across the ring in the cyclic structure **7** relative to **6** and, indeed, deshielding effects are observed. The chair conformation proposed for **7** on the basis of models and X-ray crystallography¹⁶ makes it possible to compute the parameters R and θ with rather good accuracy. The carbons marked γ fall in the shielding zone where the contours are narrowly spaced and close to the boundary where deshielding should begin. As a result, one cannot very confidently predict what should happen. That a substantial deshielding should occur is plausible, even if not gratifying. Strong shielding is predicted for the carbons marked δ of **7** from the triple bonds across the ring, and this is in accord with experiment. However, it is predicted from the curves of Figure 4 that the across-ring deshielding of the carbons marked α and β

(16) Footnote c, Table I.

would be substantially smaller in magnitude than the shielding of the carbons marked δ .

Turning now to the next pair (B) of Table III, we see that the differences between the chemical shifts of carbons α , β , and γ in the cyclic (**9**) and acyclic (**8**) examples fall in the same pattern but are smaller than in the first pair above. This attenuation would be expected from increasing R .

Pair C (Table III) is somewhat different. Here, molecular models suggest that R could be so large that neighboring-group anisotropy effects would be quite small for **11**. In fact, however, there is only a small effect on ^{13}C and it is difficult to find a reasonable arrangement of the triple bonds which gives slight shielding for ^{13}C , deshielding for ^{12}C , and nothing at ^{13}C . Something approximating this is possible if the crossing triple bonds on the average lie parallel to one another, equilibrating between two (quite reasonable) conformations with the centers of the pairs of multiple bonds staggered by about 2 Å. It is also possible that



the conjugated bonds of **11** are skewed with respect to one another. In the absence of detailed conformational data, these explanations are at best speculative.

The carbons labeled δ and ϵ in Table III show considerable shielding effects for ^{13}C of **7** and ^{13}C of **11** and this is in accord with the predictions of Figure 4. The other pairs of Table II, as expected, show little differences in shift between the cyclic and acyclic substances because in the cyclic cases, the triple-bond segments are either away from one another or held at angles such that effects will be small.

Finally, we should note an additional problem evident in earlier studies.⁵⁻⁷ Numerous proton nmr studies of alkynes have been used to derive empirical values for $\Delta\chi$ of eq 1.¹⁷ These values predict carbon chemical-shift differences that are rather too small^{6,7} and the same problem is encountered here. Similar difficulties have been found for fluorine shifts,¹⁸ and it has been suggested that electric fields should be taken into considerations in theoretical evaluations of fluorine chemical shifts.¹⁸ Certainly, electric-field effects appear to be important in carbon chemical shifts, but they have been involved only in cases where there exists a large electric dipole within the molecule.^{19,20}

Cycloalkenes.—Also included in Table II are some preliminary data for three cycloalkadienes. These substances have the advantage that their corresponding cmr spectra are frequently easier to interpret than those of corresponding acyclic compounds. However,

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(19) W. McFarlane, *Chem. Commun.*, 418 (1970).

(20) P. S. Pregosin and E. W. Randall, *ibid.*, 399 (1971).

it is apparent from Table II that even the resonances of the cyclic diene spectra are difficult to assign when the ring is large. In the case of *cis,cis*-cyclotetradeca-1,8-diene (**16**), for example, only the resonances of the trigonal and the adjacent sp^3 carbons could be assigned.

In Table IV, the cmr spectra of the cyclic dienes and model compounds are compared in the same way as for

TABLE IV
COMPARISON OF SPECTRA OF
CYCLOALKADIENES AND CYCLOALKENES^a

[C=C-C]		δ_α	δ_β
A	[Cyclohexa-1,4-diene (14) Cyclohexene ^b]	+2.7	-0.6
B	[Cycloocta-1,5-diene (15) <i>cis</i> -Cyclooctene]	+1.5	-2.6
C	[Cycloocta-1,5-diene (15) <i>cis,cis</i> -Octa-2,6-diene ^a]	+1.8	-1.3
D	[<i>cis,cis</i> -Cyclotetradeca-1,8-diene (16) <i>cis</i> -Cyclotridecene ^c]	+1.1	-0.7

^a Tabulated shift differences were obtained by subtracting the cmr spectrum of the second member of a pair from the first.

^b Reference 21. ^c Reference 11.

the alkynes. It is seen that in cyclohexa-1,4-diene, for example, the trigonal carbons have shifts at rather higher fields than is normal for *cis* alkenes.²¹ Specifically, these carbons come into resonance at a position 2.7 ppm upfield from the analogous carbons of cyclohexene. The effect at the adjacent sp^3 carbon, on the other hand, is deshielding. Comparisons of the spectra of larger cycloalkadienes with model compounds show that the shielding effect at the trigonal carbons is attenuated, while the shift differences at the directly connected sp^3 carbons are irregular.

The available evidence indicates that the diamagnetic anisotropy of the double bond results in shielding in the regions above and below the plane of the trigonal carbons, as well as possible deshielding within the plane.²² Such anisotropy should result in deshielding at the immediately adjacent sp^3 carbons. In fact, such an effect has been noted only for *trans* alkenes, and the deshielding in these cases could be an effect of electronegativity. In *cis* examples, the chemical shifts of the α carbons show a strong shielding tendency, presumably owing to steric effects.²¹ At the present time, it is not possible to identify with certainty any anisotropy effect on the α -carbon resonances.

The data in Table IV are consistent, however, with the postulated shielding effect in the region perpendicular to the plane of the double bond. Thus, the unusually high field resonance of the trigonal carbons of cyclohexa-1,4-diene could result from such an effect. This shielding effect is attenuated in the larger rings, but still seems to persist in cyclotetra-1,8-diene (**16**).

Cycloallenes.—The cyclic allenes have been studied previously by both infrared and proton nmr spectroscopy.²³ It was concluded in this earlier work that the nine-membered cyclic allene **17** was significantly

more strained than the higher homologs. The greatest differences were found to occur in the chemical shift of the protons attached to the trigonal carbons, and in the infrared band assigned to the torsional movement of the terminal carbons of the allenic unit. There appeared to be little change in the infrared band assigned to stretching vibrations of the allene.

The carbon chemical shifts reported in the present work provide some information regarding the effects of such strain on the central carbon of the allene. Thus, comparison of the spectrum of **17** with that of cyclotrideca-1,2-diene (**20**), which is considered to be relatively strain-free,²³ shows that all three carbons of the allene unit are deshielded by the effects of strain (pair A, Table V). As in the cases of *cis* and *trans* cyclo-

TABLE V
COMPARISON OF THE CMR SPECTRA OF SELECTED CYCLIC ALLENES^a

	A B C			δ_A	B	δ_C
	C-C=C=C-C					
A	[Cyclonona-1,2-diene (17) Cyclotrideca-1,2-diene (20)]	-1.3	-0.9	0.1		
B	[Cyclonona-1,2,6-diene (18) Cyclotrideca-1,2-diene (20)]	-1.5	+1.3			
C	[Cyclodeca-1,2,6,7-tetraene (19) Cyclonona-1,2-diene (17)]	-1.8	+2.5	+1.1		
D	[Cyclodeca-1,2,6,7-tetraene (19) Cyclohexadeca-1,2,9,10-tetraene (21)]	-2.6	+0.4	+3.0		
E	[Cyclohexadeca-1,2,9,10-tetraene (21) Cyclotrideca-1,2-diene (20)]	-0.5	+1.2	-1.8		

^a Tabulated shift differences were obtained by subtracting the cmr spectrum of the second member of the pair from the first.

alkenes,¹¹ the effects of strain on carbon chemical shifts seem to be small.

Ring strain may also be an important effect in the remaining comparisons shown in Table V. Unfortunately, these comparisons are further complicated by the possibility of the anisotropic shift effects arising from the alkene and allene units. The effects of the diamagnetic anisotropy of the double bond was considered above. It is possible that the increased shielding of the terminal carbons of the alkene unit of cyclonona-1,2,6-triene (**18**) relative to the simple allene **17** is due to the diamagnetic anisotropy of the double bond. Such an explanation does not account, however, for the rather little change observed in the chemical shift of the quaternary carbon (*cf.* Table II). Again, it is necessary to recognize that the additional double bond of **18** may add significantly to the strain of the ring.

The anisotropy of the allene moiety is also difficult to assess. On the basis of recently reported data for the acyclic allenes,^{24,25} one can predict that the ¹³C chemical shifts of the sp and sp^2 carbons of the allene group would be about -12 and 104 ppm, respectively. From Table II it can be seen that the chemical shifts for cyclic allenes are similar to these estimates. The case of cyclodeca-1,2,6,7-tetraene (**19**) suggests the possibility of deshielding regions immediately surrounding the sp -hybridized carbons. This idea is supported by comparisons C-E of Table V, which also suggest a complementary shielding region around the remainder of the allene unit. There are two indications, however,

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that the effect of diamagnetic anisotropy in allenes is small. First, there appears to be no large effect which can be ascribed to anisotropy at the α position. Indeed, the rather irregular chemical-shift changes which do occur at this position may be due largely to the effects of the conformation of the ring. Second, the chemical shift of the alkene carbons of *cis*-cyclononene¹¹ do not differ significantly from that of the alkene unit of cyclonona-1,2,6-triene.

Conclusions

The present results generally confirm and extend earlier conclusions⁵⁻⁷ regarding the magnetic anisotropy of the triple bond. The shifts observed show variations which are in general accord with the McConnell equation. However, the observed shifts are

several times larger than those observed in proton chemical shifts.

The carbon spectra of the alkenes and allenes do not show large effects which can unambiguously be assigned to magnetic anisotropy. Owing to limitations of the theoretical models of such systems and to the sparse data from proton nmr studies of these compounds, the recognizable effects which do occur are difficult to evaluate and assign to specific causes.

Registry No.—1, 871-84-1; 2, 16387-71-6; 3, 5601-68-3; 4, 872-21-9; 5, 1540-80-3; 6, 39805-79-3; 7, 7158-20-5; 8, 14538-94-4; 9, 4634-66-6; 10, 39805-82-8; 11, 39805-83-9; 12, 6675-65-6; 13, 39805-85-1; 14, 628-41-1; 15, 111-78-4; 16, 6108-60-7; 17, 1123-11-1; 18, 1502-42-7; 19, 3451-55-6; 20, 5601-67-2; 21, 7129-53-5.

Cycloaddition of Diphenylketene to Some C=N Heterocycles. Structural Assignment and Reactions of Adducts¹

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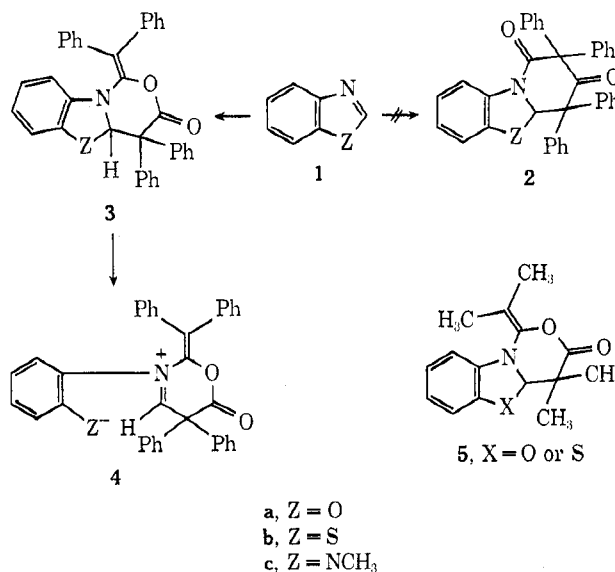
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The cycloaddition reactions of diphenylketene to some C=N heterocycles have been reexamined and the adducts are assigned oxazinone (3 or 4) rather than amido ketone structures 2. The reaction of 4 with hydrazine yielded pyrazolinone 7, whereas sodium methoxide produced the ring-opened ester 6.

As part of our interest in the cycloaddition reactions of ketenes to olefins and to heterocycles,² we investigated the reaction of some heterocyclic imines with diphenylketene.

The cycloaddition of ketenes to imines is known to proceed with formation of 1:1 or of 2:1 adducts. In the latter case six-membered ring products were isolated and assigned structures that ranged from amido ketones³ or lactones (oxazinones)⁴ to dioxazines.^{2d} The factors influencing the type of cycloadduct formed have not been examined.

The reactions of diphenylketene with 2-methylthiazoline, *N*-methylimidazole, benzoxazole, benzothiazole, and *N*-methylbenzimidazole were reported by Kimbrough,³ who found that these heterocycles added to diphenylketene in a 1:2 ratio to give adducts to which he assigned an amido ketone structure, *e.g.*, 2. These results are surprising in view of the formation of oxazinones from the cycloaddition of dimethylketene with C=N heterocycles.⁴ The infrared bands at 1770 cm^{-1} reported by Kimbrough for the adducts from benzoxazole and benzothiazole do not agree with an amido ketone structure 2. Such adducts are expected to show two strong carbonyl bands at 1710 and 1680 cm^{-1} . In the course of our cycloaddition studies of



diphenylketene we reexamined the reported reactions and would like to correct the previous structure assignment and to shed light on some interesting ring-opening reactions that occur in these heterocyclic systems.

Results and Discussion

We were able to reproduce the cycloaddition of diphenylketene to the heterocycles stated above including the infrared data. The diphenylketene adducts from benzoxazole and benzothiazole (1, Z = O and S) showed strong carbonyl absorptions at 1770 cm^{-1} and medium bands at 1665 and 1640 cm^{-1} , in addition to strong bands at 1130 cm^{-1} indicative of a

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