(15) Identification of the 3,14-diacetate as the minor component was based on a ^{1}H NMR examination of the mixture.
(16) H. Rapoport, D. R. Baker, and H. N. Reist, *J. Org. Chem.*, **22,** 1489 (1957).
(17) All of the acetate derivatives were purified by preparative chromatography on silica gel plates and were analyzed initially by infrared ($CHCl_3$ solution) on a Perkin-Elmer 467 spectrometer. The carbonyl bands of the 3-acetoxyl groups appeared in the 1754–1758-cm^{-1} region while those of the 6- and 14-acetoxyl groups appeared at 1725–1730 cm^{-1}.
(18) S. Okuda, S. Yamaguchi, Y. Kawazoe, and K. Tsuda, *Chem. Pharm. Bull.*, **12,** 104 (1964).
(19) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, Oxford 1969, p 176.
(20) We also observed that two of the methyl chemical shifts reported by Hahn and Fishman[11] differed significantly from our values, a fact which could indicate sample deterioration. In addition, we have observed that most of the acetate derivatives which we prepared would slowly decompose if left in solution.
(21) The theoretical 5β-6 values referred to were actually derived[18] for the 7,8-dihydroisomorphine and the 7,8-dihydromorphine ring systems. However, an examination of Dreiding models indicated that introduction of a 14-hydroxyl group should have little effect on these values.
(22) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 167.
(23) See, for example, the spectrum of cyclohexyl acetate (no. 311) in L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972.
(24) Reference 23, p 169.
(25) Cone and co-workers[9] have reported that the 6-hydroxyl group of **3a** is incompletely acylated with this reagent.
(26) S. H. Grover, J. P. Guthrie, J. B. Stothers and C. T. Tan, *J. Magn. Reson.*, **10,** 227 (1973).
(27) S. H. Grover and J. B. Stothers, *Can. J. Chem.*, **52,** 870 (1974).
(28) H. Eggert, C. L. VanAntwerp, N. S. Bhacca, and C. Djerassi, *J. Org. Chem.*, **41,** 71 (1976).

Carbanions. 2.[1] Carbon-13 Nuclear Magnetic Resonance Study of Meisenheimer Complexes and Their Charge Distribution Pattern

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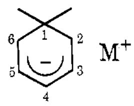
A series of 6-X,2,4-dinitroanisoles and their carbanionic methoxide addition products (Meisenheimer complexes) have been examined by ^{13}C NMR spectroscopy. Variation of X (CF_3, H, Cl, F, CH_3) does not affect the charge distribution pattern in the complexes as reflected by their ^{13}C NMR shifts. Only in the case where X is NO_2 can a change be observed. The ^{13}C NMR studies indicate that the cyclohexadienylic carbons carry about 0.3–0.4 e more negative charge than the corresponding carbons in their aromatic precursors. The additional charge is located on C_2, C_4, and C_6.

Intensive studies on the interaction of electron-deficient aromatic compounds with alkoxides culminated in 1902 with Meisenheimer's evidence that these complexes could be described by the structural formula 1.[2] These complexes, however, attracted little attention until 1964 when Crampton and Gold reported the first ^{1}H NMR spectrum of a Meisenheimer complex.[3a] Since then, numerous papers on the ^{1}H NMR studies of these complexes have been published,[3b] some of which also discussed aspects of their charge distribution pattern.[4] However, electron-withdrawing groups must occupy at least two and often three of the positions ortho and para (i.e., 2, 4, and 6) to the aliphatic center 1 in order to obtain stable complexes. As a result, the ortho and para positions, which are expected to carry most of the negative charge in cyclohexadienyl anions, cannot be studied by ^{1}H NMR spectroscopy, and the limitations of the ^{1}H NMR method of investigating charge distributions become evident.



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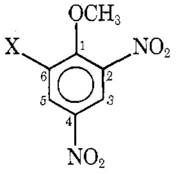
We now wish to report the first ^{13}C NMR spectroscopic study of Meisenheimer complexes, in which the obvious limitations of the ^{1}H NMR method are absent.

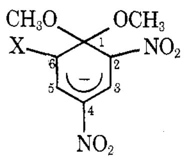
Results[5]

Substituted Anisoles. All ^{13}C NMR spectra showed a high-field absorption close to δ_C 65 (Table I), which was assigned to the methoxyl carbon based on the chemical shift and its quartet splitting in off-resonance spectra. Furthermore, off-resonance experiments allowed the separation of the C_3 and C_5 shifts from the other carbon shifts. δ C_3 and C_5 were found to be identical in anisoles **2** and **3**. In **6** these carbon shifts were characterized on the basis of the C–F couplings (J_{C_5F} = 14, J_{C_3F} = 8 Hz). In all other cases C_3 and C_5 were separated by more than 10 ppm, and their assignments were made possible by comparison of the observed shifts with calculated shifts.[6] The observed shifts showed a maximum deviation of 3.1 ppm from those which were determined from the substituent increments in monosubstituted benzenes.[6]

In accord with the calculations the most deshielded peaks were always ascribed to C_1. The only exception was **6** where C_6 was most deshielded, as indicated by the calculations and experimentally proved by its CF coupling of 231 Hz. The resonance at δ_C 127.6 was the only sp^2 carbon absorption of **3** showing CF coupling (6 Hz) and therefore could be assigned to C_6. Though the similarity between the calculated and observed C_1 and C_6 shifts in **5** and **7** is not outstanding, comparison with the resonances of the other singlets shows that no other assignment is possible.

In general, the nitro-substituted positions C_2 and C_4 show only slightly different chemical shifts. Though their assignments were not crucial to our present study, it was attempted on the basis of their intensities. If C_6, C_2, and C_4 in **2** had the





X		
NO_2	**2**	**2a**
CF_3	**3**	**3a**
H	**4**	**4a**
Cl	**5**	**5a**
F	**6**	**6a**
CH_3	**7**	**7a**

Table I. ^{13}C NMR Shifts of 2,4-Dinitro-6-X-anisoles at 15.1 MHz in $CDCl_3$ with Me_4Si as External Standard, Calculated Shifts[6] in Parentheses

Compd[a]	X	C_1	C_2	C_3	C_4	C_5	C_6	OCH_3	Other
2	NO_2	153.1	145.6	125.3	142.5	125.3	145.6	66.4	
		(156.1)	(135.9)	(125.7)	(142.6)	(125.7)	(135.9)		
3	CF_3	158.1	144.1	126.2	142.6	126.2	127.6	65.4	122.5
		(158.7)	(135.3)	(123.1)	(142.0)	(128.3)	(114.9)		(J = 274 Hz)
4	H	158.5	139.5	122.6	141.7	130.4	115.2	58.7	
		(160.9)	(135.0)	(119.9)	(141.7)	(130.5)	(106.9)		
5	Cl	155.8	145.4	120.3	143.4	130.2	132.6	64.2	
		(161.3)	(136.3)	(118.0)	(143.0)	(130.9)	(122.1)		
6	F	147.3	141.8	117.0	144.1	117.9	156.2	64.0	
		(148.0)	(136.4)	(115.4)	(143.1)	(117.6)	(150.7)		
7	CH_3	157.5	144.0	119.7	143.1	130.5	137.6	63.4	17.5
		(161.6)	(134.9)	(117.0)	(141.6)	(131.2)	(124.8)		

[a] Respective registry numbers are 606-35-9, 320-16-1, 119-27-7, 23789-10-8, 344-78-5, 29027-13-2.

Table II. ^{13}C NMR Shifts of 1,1-Dimethoxy-2,4-dinitro-6-X-cyclohexadienyl Anions at 25.16 MHz in Me_2SO-d_6 with Me_4Si as External Standard[a]

Compd[b]	X	C_1	C_2	C_3	C_4	C_5	C_6	OCH_3	Other
2a	NO_2	104.3 (s)	129.2 (s)	131.2 (d)	119.3 (s)	131.2 (d)	129.2 (s)	53.2 (q)	
	NO_2[c]	103.9	129.2	130.0	118.8	130.0	129.2	52.8	
3a	CF_3	104.8 (s)	123.5 (s)[d]	131.8 (d)	119.8 (s)[d]	129.7 (dq)	111.3 (q)	52.6 (q)	125.7 (q)
4a	H	104.1 (s)	122.9 (s)	131.1 (d)	121.7 (s)	125.4 (d)	118.5 (d)	52.0 (q)	
5a	Cl	104.9 (s)	121.2 (s)[d]	130.5 (d)	120.6 (s)[d]	126.0 (d)	120.7 (s)[d]	52.5 (q)	
6a	F	103.7 (d)	121.2 (d)	128.8 (d)	118.4 (d)	107.8 (dd)	148.3 (d)	52.8 (q)	
7a	CH_3	106.0 (s)	120.7 (s)	130.9 (d)	122.6 (s)	123.9 (d)	125.4 (s)	52.0 (q)	16.7 (q)

[a] Multiplicities refer to one-bond CH couplings and all fluorine couplings. [b] Respective registry numbers are 12128-30-2, 33516-46-0; 12128-33-5, 25230-80-2, 33542-12-0, 59906-98-8. [c] 1:1 complex with 18-crown-6 ether dissolved in THF. [d] Assignments uncertain; see text.

same relaxation time, a 2:1 intensity ratio should have been observed. We detected, however, two signals of equal intensity and concluded that C_4 was relaxing faster. Using a lower pulse width resulted in an increase of intensity of the δ_C 145.6 peak relative to that at δ_C 142.5 and the latter was identified as C_4. Generalizing this observation to the anisoles 3–7 we ascribed the less intensive resonance of the nitro-substituted carbons to C_2.

Meisenheimer Complexes. All spectra were characterized by a quartet absorption around δ_C 52 and a singlet around δ_C 104, which were assigned to the methoxy carbon and C_1, respectively (Table II).

The trinitro compound **2a** with C_{2v} symmetry showed a doublet at δ_C 131.2 (C_3, C_5) and two singlets at δ_C 129.2 (C_2, C_6) and 119.3 (C_4), which could be assigned due to their 2:1 ratio of intensities.

In **3a** the quartet at δ_C 111.3 (J_{CF} = 27.6 Hz) was ascribed to C_6. A smaller CF coupling (J_{CF} = 6 Hz) was also detected in the signal at δ_C 129.7 which, in addition to the off-resonance experiments, allowed attribution to C_5. While the off-resonance splitting of the δ_C 131.8 resonance also revealed C_3, the assignment of C_2 and C_4 was not directly possible. As shown below, the C_4 shift was found to be almost constant in all systems. Therefore, C_4 was tentatively ascribed to the resonance at δ_C 119.8 and C_2 to that at δ_C 123.5.

4a showed three carbons attached to hydrogen at δ_C 118.5, 125.4, and 131.1; the highest field signal was attributed to C_6. A trace of CH_3O^-, added to the solution of **4a** in Me_2SO-d_6, caused a slow decrease of the signal at δ_C 131.1 while all other peaks remained unchanged. This observation was interpreted as an exchange of 3-H by deuterium.[7] The fact that no change in the NMR spectrum was observed in Me_2SO/CH_3O^- solution emphasizes the above explanation. The doublets at δ_C 125.4 and 131.1, therefore, could be assigned to C_5 and C_3, respectively. In the proton-coupled spectra the signal at δ_C 122.9 was split into a doublet and was assigned to C_2, since a different splitting pattern had to be expected for C_4. The observation of the proton coupled C_4 was not possible because its signal overlapped with C_6 and C_5.

The three singlets assigned to C_2, C_4, and C_6 of **5a** were in such close proximity that they could not be ascribed specifically. Since the C_3 shielding is relatively constant in all systems, it was assigned to the doublet at δ_C 130.5 and the remaining doublet at δ_C 126.0 to C_5.

In **6a** the signal at δ_C 128.8 was the only ring carbon that did not show fluorine coupling and therefore was assigned to C_3. C_6 was coupled to fluorine with a coupling constant of 258 Hz while C_1 and C_5 displayed coupling constants of 23 Hz. Since the signals of C_2 and C_4 were doublets with the same CF coupling constant of 11 Hz, the proton-coupled carbon spectrum was necessary for their assignments. The resonance at δ_C 121.2 was then split by one hydrogen (J_{CH} = 4 Hz) and assigned to C_2 while the resonance at δ_C 118.4 was coupled to two hydrogens (J_{CH} = 4 Hz) and assigned to C_4.

In **7a** long distance couplings allowed the assignment of the resonances at δ_C 123.9 and 130.9 to C_5 and C_3, respectively. The C_3 resonance at δ_C 130.9 was split by its adjacent hydrogen with a coupling of 164 Hz, and by H_5 with a coupling constant of 4 Hz. In addition to the corresponding couplings, C_5 was also split by the methyl group resulting in a pair of quintets, one of which coincided with C_2. In the coupled spectrum the resonance at δ_C 125.4 appeared as a distorted quintet in which both CH_3 and H_5 were coupled similarly to C_6. Finally the doublet of 5 Hz at δ_C 120.7 was ascribed to C_2. The expected triplet splitting of C_4 by H_3 and H_5 was only observed as a broad line.

Discussion

Substituted Anisoles. Table I shows an excellent agreement between calculated and observed shifts of the positions C_3, C_4, and C_5. Since the maximum deviation found is 3.1 ppm, the additivity of the substituent effects[6] is well demonstrated. In the case of C_1 the maximum deviation becomes 5.5 ppm. The correspondence between the calculated and observed

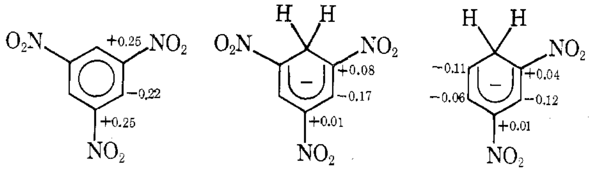


Figure 1. Calculated π-electron charges.[9]

shifts, however, is poor for C_2 and C_6. A difference of 10 ppm is frequently observed. Since C_6 as well as C_2 are more deshielded than expected from the calculations, the reason might be the steric inhibition of resonance of the methoxyl group.

This is stressed by the fact that the calculated and observed values agree very well in the case of the hydrogen substituted compound **4**, in which a planar conformation of the methoxyl group can be achieved. On the other hand, it is not clear why the agreement is so close for C_4, as the distorted coplanarity of the methoxyl group should also affect that position.

Meisenheimer Complexes. In structurally similar molecules a linear correlation between ^{13}C NMR shifts and charge densities can be expected, particularly if relatively small charges are considered.[8] In the complexes **2a–7a**, therefore, the chemical shifts of C_2, C_3, and C_4 should reflect the relative electron density as they are separated from the substituent X by three or four bonds.

MO and resonance theory predict that C_3 will not carry any significant charge in cyclohexadienyl ions and the constancy of this shift (Table II) thus is not surprising. On the other hand the C_4 shielding also remains unchanged while C_2 experiences a deshielding as the electron-withdrawing ability of X increases. These results support SCF MO calculations by Wennerström[9] (Figure 1). While a π-electron charge of +0.01 was calculated for C_4 of both the 2,4-dinitrocyclohexadienyl anion and the 2,4,6-trinitrocyclohexadienyl anion, the positive charge of +0.08 at C_2 of the trinitrocyclohexadienyl anion decreases to +0.04 in the dinitro compound. The difference of 0.04 ppm corresponds to 6.4 ppm if the slope of the correlation line is accepted to be 160 ppm per electron charge.[8] The coincidence of this value with the observed difference between the C_2 resonances of **2a** and **4a** is regarded to be accidental.

Data of Table II furthermore show that, disregarding a small effect of CF_3, only NO_2 exerts a considerable deshielding of C_2. The ^{13}C NMR data, therefore, demonstrate that NO_2 stabilizes the negative charge much better than CF_3. This conclusion is supported by the fact that neither 2-methoxy-5-nitrobenzotrifluoride nor 4-methoxy-3-nitrobenzotrifluoride show a color change when treated with $^{-}OCH_3$ (indicative of formation of Meisenheimer complex), while 2,4-dinitroanisole (4) yielded the crystalline complex **4a**.

To ascertain that the observed chemical shifts of the anions are not influenced by a significant ion pairing effect,[10] the ^{13}C NMR spectrum of **3a** was also recorded in the presence of 18-crown-6 ether. Table II shows that the deviations are less than 1.2 ppm and can be thus neglected.

Comparison between Meisenheimer Complexes and Their Precursors. HMO calculation led to the conclusion that the addition of alkoxides to polynitrobenzenes causes a decrease of negative charge on the ring carbons.[11] Because this conclusion contradicted more elaborate quantum mechanical calculations,[9,12] we compared the ^{13}C shifts of the studied Meisenheimer complexes with their precursors (Table III).

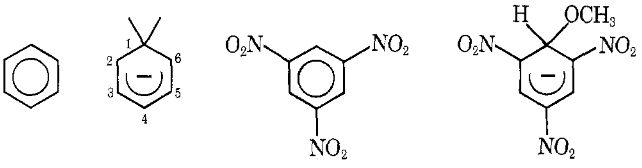
First it is necessary to evaluate the importance of factors other than charge densities that might influence the chemical shifts.

Comparing the shieldings of the sp^2 carbons in benzene, 1,3-cyclohexadiene, and cyclohexene,[13] it becomes obvious that the replacement of a CH group in benzene by CH_2 does not significantly affect the shifts of the other olefinic carbons.

Table III. Differences between the ^{13}C NMR Shifts of the Meisenheimer Complexes 2a–7a and the Anisoles 2–7

X	C_2	C_3	C_4	C_5	C_6	Sum
NO_2	−16.4	+5.9	−23.2	+5.9	−16.4	−44.2
CF_3	−20.6	+5.6	−22.8	+3.5	−16.3	−50.6
H	−16.6	+8.5	−20.0	−5.0	+3.2	−29.9
Cl	−24.2	+10.2	−22.8	−4.2	−11.9	−52.9
F	−20.6	+11.8	−25.7	−10.1	−7.9	−52.5
CH_3	−23.3	+11.2	−20.5	−6.6	−12.2	−51.4

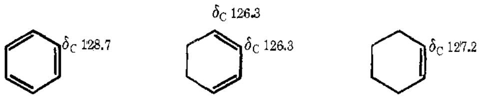
Table IV. ^{13}C NMR Shifts of the Compounds 8, 8a, 9, and 9a



8 **8a** **9** **9a**

	C_2	C_3	C_4	C_5	C_6	Sum
8[a]	128.7	128.7	128.7	128.7	128.7	
8a[b]	75.8	131.8	78.0	131.8	75.8	
Δ(8a/8)	−52.9	+3.1	−50.7	+3.1	−52.9	−150.3
9[c]	149.5	125.2	149.5	125.2	149.5	
9a[d]	132.6	127.0	122.2	127.0	132.6	
Δ(9a/9)	−16.9	+1.8	−27.3	+1.8	−16.9	−57.5

[a] Reference 13, p 95. [b] In NH_3 at −70 °C. [c] In $CDCl_3$. [d] In Me_2SO/CH_3OH.



Therefore, it is concluded that the change in carbon shifts between benzene and the cyclohexadienyl anion is almost entirely due to charge effects (Table IV). In fact, the observed shielding of 150 ppm is very close to that predicted by the Spiesecke–Schneider relationship for the shielding of aromatic carbons by one electron (160 ppm).[8]

The comparison of **2a** with **9a** furthermore shows that the replacement of OCH_3 by H at C_1 results in a deshielding for C_2, C_6 (+3.4 ppm), and C_4 (+2.9 ppm) and a shielding for C_3 and C_5 (−4.2 ppm). These effects sum up to 1.3 ppm for all carbons C_2 to C_6 and can be thus neglected. Consequently it is possible to compare the total shieldings of the olefinic carbons in different cyclohexadienyl anions irregardless of their substitution at C_1 by H or OCH_3.

In contrast to the 150-ppm shielding which accompanies the formation of the cyclohexadienyl anion from benzene,[14] the addition of methoxide to trinitrobenzene results in an additional shielding of only 57 ppm. Since it is improbable that the approximations made during this derivation influence this large difference significantly, we can conclude that the electron density of the olefinic carbons in **9a** is increased by ~0.4 e relative to the precursor **9**, while ~0.6 e is absorbed by the nitro groups. This value is similar to the 0.48 e increase of negative ring charge predicted by SCF MO calculations (Figure 1). On the other hand, the inability of the HMO method[11] to treat problems of this kind is demonstrated.

The formation of the σ complexes from **5**, **6**, and **7** results in an additional shielding of 52 ppm (Table III). Almost the same result is observed in the CF_3 system and a noteworthy difference is found only for the trinitro compound **2** (44 ppm). The smaller increase of electron density on the carbon atoms of **2a** again demonstrates the exceptional ability of NO_2 to attract electrons. As discussed earlier, the electron density released by the coplanar methoxyl group is more effective in dinitroanisole (**4**) than in the other trisubstituted anisoles **3–7**. Since the mesomeric effect of the OCH_3 group is lost in the σ complexes, the relatively small increase of shielding from **4** to **4a** can be explained.

The difference between the pairs **2**/**2a** (44 ppm) and **9**/**9a** (57 ppm) can be interpreted analogously. While the average shifts of the complexes **2a** and **9a** are identical, the carbons 2–6 carry more negative charge in the trinitroanisole **2** than in trinitrobenzene **9**, in which the electron-releasing OCH_3 group is missing.

Disregarding **4** because of its special properties, the data of Table III reveal some other systematic trends. It is obvious that in all systems, C_2 and C_4 and to a minor degree also C_6 experience the increase of electron density as a consequence of the added methoxide ion forming the Meisenheimer complex. The deshielding which is observed for C_3 is also reflected by SCF MO calculations (Figure 1). The effects in C_5 are not yet clearly understood.

Conclusion

In 6-X,2,4-dinitrocyclohexadienyl anions ($X = CH_3$, Cl, F, H, CF_3) the variation of substituent X has almost no effect on the overall charge distribution. Only in the case of $X = NO_2$ is a difference observed, demonstrating the superior ability of the NO_2 group in stabilizing negative charge.

The ^{13}C NMR data do not allow a conclusion about the absolute charge distribution in anionic σ complexes. They do demonstrate, however, that the cyclohexadienylic carbons carry about 0.3–0.4 e more negative charge than the corresponding positions in their aromatic precursors. The additional charge is located on C_2, C_4, and C_6, while the other positions remain unchanged or even experience a small deshielding effect.

Experimental Section

Anisoles. Trinitroanisole (**2**) and 2-methoxy-3,5-dinitrobenzotrifluoride (**3**)[15] (bp 128–130 °C, 0.25 Torr) were readily prepared in the usual manner by treating picryl chloride and 2-chloro-3,5-dinitrobenzotrifluoride with $NaOCH_3$. The anisoles **5**[16] (bp 128–131 °C, 0.05 Torr), **6**[17] (bp 118–120 °C, 0.025 Torr), and **7**[18] (mp 68–70 °C) were prepared by nitration of the O-substituted anisoles according to literature procedures. All other compounds were commercially available.

Preparation of Meisenheimer Complexes. **2a**–**7a** were prepared as crystalline compounds in analogy to the procedure described for the preparation of **4a**.[4c] In contrast to the other complexes **2a**–**7a**, **4a** was not stable in Me_2SO solution. However, addition of a trace of CH_3O^-/CH_3OH to the Me_2SO stabilized the ion and allowed its NMR spectra to be obtained. A stable solution of **9a** was prepared by adding a solution of $KOCH_3$ (2.1 mmol) in CH_3OH to trinitrobenzene (2.0 mmol) dissolved in Me_2SO. Addition of 18-crown-6 ether to a solution of **2a** in Me_2SO yielded a crystalline precipitate, identified as a 1:1 complex of **2a** and 18-crown-6 ether by integration of its ^1H NMR spectrum. Since the solubility of the complex in Me_2SO was bad, it was dissolved in tetrahydrofuran for the examination of the NMR spectra. The reaction of 1,4-cyclohexadiene with KNH_2 in NH_3 at −78 °C yielded a solution of the cyclohexadienyl anion, contaminated by a trace of benzene.[19] The solution was stable at −70 °C, at which temperature the spectrum was taken.

Carbon-13 Magnetic Resonance Spectra. The spectrometers used were Varian Associates Model XL-100 and a modified HA-60 equipped with a broad-band decoupler and a variable temperature probe.

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Registry No.—**8**, 110-82-7; **8a**, 27900-34-1; **9**, 99-35-4; **9a**, 12244-65-4.

References and Notes

(1) For part 1, see R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Am. Chem. Soc.*, **88**, 1272 (1966).
(2) J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **323**, 205 (1902).
(3) (a) M. R. Crampton and V. Gold, *J. Chem. Soc.*, 3293 (1964). (b) For a review see M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).
(4) (a) F. Terrier, J-C. Halle, and M-P. Simonnin, *Org. Magn. Reson.*, **3**, 361 (1971); (b) M. P. Simonnin, M. J. Lecourt, F. Terrier, and C. A. Dearing, *Can. J. Chem.*, **50**, 3558 (1972); (c) W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **32**, 2506 (1967).
(5) If not otherwise mentioned, multiplicities refer to one-bond hydrogen and all fluorine couplings.
(6) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience, New York, N.Y., 1972, p 81.
(7) R. J. Pollit and B. C. Saunders, *Proc. Chem. Soc., London*, 176 (1962); E. Buncel and E. A. Symons, *Can. J. Chem.*, **44**, 771 (1966); M. R. Crampton and V. Gold, *J. Chem. Soc. B*, 498 (1966).
(8) D. G. Farnum, *Adv. Phys. Org. Chem.*, **11**, 123 (1975).
(9) H. Wennerström and O. Wennerström, *Acta Chem. Scand.*, **26**, 2883 (1972).
(10) M. R. Crampton, *J. Chem. Soc., Perkin Trans. 2*, 825 (1975).
(11) P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, **50**, 848 (1967).
(12) H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, **12**, 117 (1968).
(13) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 77.
(14) There is some evidence that the resonances of **8a** are somewhat shifted to high field because of homoaromatic C_1C_5 overlap. As this effect is not expected to exceed 10 ppm, we will neglect this influence during these considerations.
(15) M. E. Friedrich and L. E. Schniepp, U.S. Patent 2 257 093 (1941).
(16) F. Reverdin and K. Philipp, *Ber. Dtsch. Chem. Ges.*, **38**, 3774 (1905).
(17) G. Schiemann and T.-B. Miau, *Ber. Dtsch. Chem. Ges.*, **66**, 1179 (1933)
(18) M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951).
(19) H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **89**, 368 (1970).