Experimental Section

Materials.—PNPA obtained from Nakarai Chemicals Co., Kyoto, Japan, was further purified by recrystallization until it was nearly colorless (mp 78°). PNPPR, PNPV, PNPC, and PNPL obtained from Sigma Chemicals Co. were used without further purification. PNPP was a guaranteed reagent from Nakarai Chemicals Co. The details about the preparation of the polymers, namely C2PVP, C4PVP, BzPVP, C16BzPVP, and DECS, were described in the preceding paper.[6] The degree of polymerization of the parent poly(4-vinylpyridine) is 3800. The characterization of NaDNA was also described before.[6] NaLS and CTABr were commercially available. Deionized water was used for the preparation of the solutions of esters and polymer catalysts.

Kinetic Measurements.—Reaction rates were obtained from the change in absorbance at 400 nm owing to release of *p*-nitrophenoxide ion. The rapid reaction was followed using a Hitachi stopped-flow spectrophotometer, Model RSP-2, with a Hitachi memoriscope Model V-018. The slow ractions were monitored using a Hitachi spectrophotometer Model EPS-3T.

Registry No.—PNPA, 830-03-5; PNPPR, 1956-06-5; PNPV, 1956-07-6; PNPC, 1956-10-1; PNPL, 1956-11-2; PNPP, 1492-30-4; C2PVP, 25619-82-3; C4PVP, 25703-28-0; BzPVP, 30109-97-8; C16BzPVP, 40780-43-6; DECS, 27577-32-8; CTABr, 57-09-0; NaLS, 151-21-3.

Proton Nuclear Magnetic Resonance Spectra of 1-Substituted Acenaphthenes and Other Systems of Well-Defined Geometry[1a]

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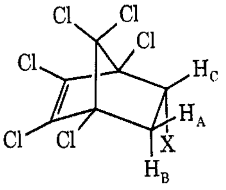
The pmr spectra of 22 1-substituted acenaphthenes were analyzed and the published nmr data for series of hexachlorobicyclo[2.2.1]heptenes, oxiranes, 1,1-dichlorocyclopropanes, and dibenzobicyclo[2.2.2]octadienes were extended by the analysis of the parent compound using ^{13}C satellites. The above data enable us to derive the following conclusions. (1) For the common range of functional groups, the dependence of vicinal and geminal coupling constants on the "electronegativity" of the substituent X is complex. However, it appears likely that empirical "substituent effects" can be used predictively. (2) A wide variety of substituents shield the vicinal protons eclipsed by them relatively to those trans to them. With some substituents ($-COCH_3$, $-COOH$, $-COOMe$, $-CONH_2$, $-N^+Me_3$, $-CHO$) the opposite effect may be observed. (3) By comparison with unsubstituted compounds, trans vicinal protons and geminal protons are deshielded by all substituents encountered here, except $-SiMe_3$. The cis vicinal protons may be either shielded or deshielded. (4) No encompassing theoretical analysis of the observed shifts was possible. However, by restricting the data to selected substituents it has been shown that the shift of the geminal hydrogen induced by a given substituent depends on the substrate. A Hammett-type relationship has been proposed which should prove useful for estimation of chemical shifts. An interpretation of this observation in terms of the inductive effect is presented. (5) For substituents limited to first-row elements, both vicinal hydrogens are shifted to about the same extent, consistent with either electric field or inductive effects. In addition, the eclipsed vicinal hydrogen shows a substantial upfield shift which is not explicable by any current theory. A new interpretation in terms of backbonding and a Karplus type relationship is suggested.

To explore the influence of substituents on chemical shifts and coupling constants, it is necessary to use molecules of reasonably well-defined stereochemistry. System **1** represents one class of compounds where H_A and H_C are approximately eclipsed and X is any substituent of interest in proton magnetic resonance studies. Clearly, system **1** can be incorporated only into flat, rigid rings and extensive systematic studies have so far been confined to hexachlorobicyclo[2.2.1]heptenes (**2**)[2a] and their 7,7-difluoro derivatives,[2b] 1,1,dichlorocyclopropanes (**3**),[3] oxiranes (**4**),[3] cyclopropanes (**5**),[4,5] and norbornenes (**6**).[6] A fairly large collection of data is also available[7] for dibenzobicyclo[2.2.2]octadienes (**7**), and some general studies dealing with the effects of substituents on coupling constants[8] are pertinent.

1



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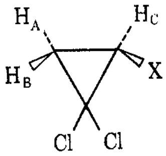

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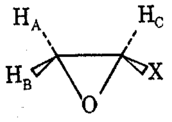

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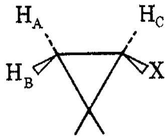

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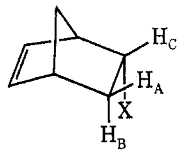

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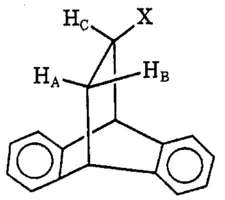

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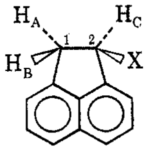

8

This work deals with the nmr parameters for fragment **1** in 22 1-substituted acenaphthenes (**8**) and with the extension of data for systems **2**, **3**, **4**, and **7** by the analysis of the nmr spectra of the parent compounds (X = H) for each series. The principal purpose of the present study was the exploration of previously pro-

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[1] (a) Abstracted in part from the Ph.D. thesis of P. W. Westerman, University of Sydney, 1970; (b) University of Sidney; (c) Purdue University; (d) Varian Associates.

[2] (a) K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963); (b) K. L. Williamson and J. C. Fenstermaker, *ibid.*, **90**, 342 (1968).

[3] K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964).

[4] K. M. Creeely, V. S. Watts, and J. H. Goldstein, *J. Mol. Spectrosc.*, **30**, 184 (1969).

[5] P. A. Scherr and J. P. Oliver, *ibid.*, **31**, 109 (1969).

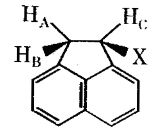
[6] P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2709 (1963).

[7] S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).

[8] S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

TABLE I

NMR DATA FOR 1-SUBSTITUTED ACENAPHTHENE DERIVATIVES[a]

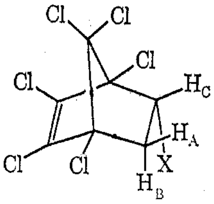


Registry no.	No.	X	E_X[b]			Chemical shifts, ppm (ex TMS)[f]				Chemical shifts from parent (X = H), ppm			Coupling constants, Hz		
			c	d	e	H_A	H_B	H_C	$\delta_A - \delta_B$	H_A	H_B	H_C	J_{AB}	J_{AC}	J_{BC}
83-32-9	1	H	1.78	2.00	1.9	3.36	3.36	3.36	0	0.0	0.0	0.0	—	9.2 ± 0.1	3.8 ± 0.1
35998-76-6	2	CMe_3[g]	2.02	2.20	2.1	3.40	3.30	3.53	0.10	−0.04	0.06	−0.17	−17.88 ± 0.02	8.25 ± 0.02	3.28 ± 0.02
18086-45-8	3	Me	2.07	2.23	2.2	3.43	2.74	3.53	0.69	−0.09	0.62	−0.17	−17.4 ± 0.2	8.1 ± 0.05	3.8 ± 0.1
40745-35-5	4	CH_2COMe	2.24	2.38	2.3	3.67	2.96	4.07	0.71	−0.31	0.40	−0.71	−17.5 ± 0.3	8.0 ± 0.3	3.5 ± 0.3
7508-18-1	5	CH_2COOH	2.25	2.38	2.3	3.69	3.10	4.11	0.59	−0.33	0.26	−0.75	−17.1 ± 0.3	8.0 ± 0.3	3.0 ± 0.3
40745-37-7	6	$CH(CO\bar{O})_2$[h]	2.35	2.47	2.4	3.71	3.15	4.33	0.56	−0.35	0.21	−0.97	−18.0 ± 0.3	8.0 ± 0.3	3.5 ± 0.3
40745-38-8	7	$CH(COOEt)_2$[i]	2.40	2.51	2.5	3.60	3.32	4.37	0.28	−0.24	0.04	−1.01	−17.8	8.6	3.2
						(3.66)	(3.31)	(4.35)	(0.35)						
40745-39-9	8	CN	2.49	2.58	2.5	3.82	3.72	4.55	0.10	−0.46	−0.36	−1.19	−17.60 ± 0.02	9.02 ± 0.03	5.14 ± 0.03
								(4.42)							
40745-40-2	9	$CONH_2$[j]	2.53	2.62	2.6	3.47	3.73	4.39	−0.26	−0.11	−0.37	−1.03	−17.57 ± 0.01	8.02 ± 0.02	3.40 ± 0.02
40745-41-3	10	COOMe	2.58	2.66	2.6	3.52	3.82	4.49	−0.30	−0.16	−0.46	−1.13	−17.8 ± 0.1	8.8 ± 0.1	4.1 ± 0.1
6833-51-8	11	COOH	2.60	2.68	2.6	3.57	3.82	4.55	−0.25	−0.21	−0.46	−1.19	−17.52 ± 0.00	8.73 ± 0.00	3.71 ± 0.00
40745-43-5	12	Ph	2.75	2.80	2.8	3.82	3.26	4.71	0.56	−0.46	0.10	−1.35	−17.51 ± 0.04	8.57 ± 0.04	4.24 ± 0.04
						(3.82)	(3.26)	(4.71)	(0.56)						
40745-44-6	13	NH_2	2.91	2.93	2.9	3.64	2.88	4.71	0.76	−0.28	0.48	−1.35	−17.42 ± 0.02	7.47 ± 0.02	3.35 ± 0.02
						(3.70)	(2.93)	(4.75)	(0.77)						
24171-73-1	14	Br	2.96	3.10	3.0	3.84	3.65	5.71	0.19	−0.48	−0.29	−2.35	−18.63 ± 0.03	7.27 ± 0.04	2.21 ± 0.04
								(5.83)							
40745-46-8	15	CPh_3[k]	3.07	3.06	3.1	3.90	3.10	5.44	0.80	−0.54	0.26	−2.08	−17.56 ± 0.07	8.28 ± 0.07	2.43 ± 0.07
40745-47-9	16	$^+NMe_3{}^-Br$[l]	3.17	3.15	3.2	3.74	3.97	5.61	−0.25	−0.38	−0.61	−2.25	−19.08 ± 0.05	8.21 ± 0.06	1.56 ± 0.06
40745-48-0	17	NHCOMe	3.21	3.18	3.2	3.89	3.08	5.92	0.81	−0.53	0.28	−2.56	−17.80 ± 0.00	7.46 ± 0.00	2.84 ± 0.00
40745-49-1	18	Cl	3.25	3.21	3.2	3.82	3.52	5.67	0.30	−0.46	−0.16	−2.31	−18.00 ± 0.00	7.37 ± 0.00	2.44 ± 0.00
						(3.99)	(3.65)	(5.80)	(0.34)						
21857-35-2	19	OMe	3.30	3.25	3.3	3.64	3.31	5.39	0.33	−0.28	0.05	−2.03	−17.80 ± 0.00	7.10 ± 0.00	2.51 ± 0.00
						(3.51)	(3.24)	(5.30)	(0.27)						
6306-07-6	20	OH	3.43	3.36	3.4	3.64	3.11	5.59	0.53	−0.28	0.25	−2.23	−17.80 ± 0.00	7.13 ± 0.00	2.57 ± 0.00
						(3.71)	(3.14)	(5.58)	(0.57)						
14966-36-0	21	OCOMe	3.74	3.60	3.7	3.68	3.18	6.50	0.50	−0.32	0.18	−3.14	−17.50 ± 0.00	7.24 ± 0.00	2.46 ± 0.00
						(3.63)	(3.19)	(6.42)	(0.44)						
3798-81-0	22	F[m]	3.92	3.76	3.9								−18.30	6.68	1.49

[a] The data refer to *ca.* 10% solutions in $CDCl_3$ unless otherwise indicated. Chemical shifts are believed to be significant to ±0.02 ppm and coupling constants to ±0.2 Hz, unless otherwise indicated. [b] The chemical shift data for ethyl derivatives EtX used to calculate the electronegativity of X (E_X) are taken from the previously prepared compilation (ref 10b) unless otherwise stated. [c] Dailey electronegativity (ref 9). [d] Muller electronegativity: J. C. Muller, *Bull. Soc. Chim. Fr.*, 1815 (1964). [e] Electronegativity value accepted in this work. [f] Figures in parentheses refer to chemical shifts in 1–3% solutions in CCl_4. [g] Chemical shifts of Me_3CCH_2Me used in calculating electronegativities were obtained from the work of Bartz and Chamberlain: K. W. Bartz and N. F. Chamberlain, *Anal. Chem.*, **36**, 2151 (1964). [h] Data for solution in D_2O containing excess potassium carbonate. Chemical shifts are from trimethylsilylpropanesodium sulfonate (TMPS). Under the same conditions the chemical shifts in $MeCH_2CH(COO^-)_2$ are δ_{Me} 0.85, δ_{CH_2} 1.67 ppm. [i] Chemical shifts in $MeCH_2CH(COOEt)_2$ are δ_{Me} 0.95, δ_{CH_2} 1.86 ppm (CCl_4 solution). [j] Approximately 5% solution in CCl_4 (90%) and DMSO (10%). [k] 1-Tritylacenaphthene [G. Wittig, W. Tochtermann, and B. Knickel, *Angew. Chem., Int. Ed. Engl.*, **7**, 139 (1968); W. Tochtermann and B. Knickel, *Chem. Ber.*, **102**, 3508 (1969)] was kindly donated by Dr. W. Tochtermann, Heidelberg. Chemical shifts in 1,1,1-triphenylpropane are δ_{Me} 0.78, δ_{CH_2} 2.66 ppm ($CDCl_3$ and CCl_4). [l] In D_2O chemical shifts from TMPS. In both diethyldimethylammonium iodide and triethylmethylammonium iodide $\delta_{Me} - \delta_{CH_2}$ = 2.04 ppm (in D_2O). [m] Data from Dr. L. D. Hall, University of British Columbia.

TABLE II

NMR DATA FOR HEXACHLOROBICYCLO[2.2.1]HEPTENES[a]

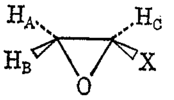


Registry no.	No.	X[i]	E_X[b]			Chemical shifts, ppm (ex TMS)				Chemical shifts from parent (X = H), ppm			Coupling constants, Hz		
			c	d	e	H_A	H_B	H_C	$\delta_A - \delta_B$	H_A	H_B	H_C	J_{AB}	J_{AC}	J_{BC}
22039-38-9	1	H	1.78	2.00	1.9	2.49	2.00	2.49	0.49	0	0	0	−12.42	9.73[f]	3.81
40745-55-9	3	CH_3[g]	2.07	2.23	2.2	2.63	1.58	2.86	1.05	−0.14	0.42	−0.37	−12.18	8.81	3.91
19095-26-2	8	CN	2.49	2.58	2.5	2.70	2.15	3.40	0.55	−0.21	−0.15	−0.91	−12.6	9.3	4.6
2157-20-2	11	COOH	2.60	2.68	2.6	2.72	2.43	3.62	0.29	−0.23	−0.43	−1.13	−12.6	8.5	4.4
17064-54-9	12	Ph	2.75	2.80	2.8	2.87	2.38	3.87	0.49	−0.38	−0.38	−1.38	−12.7	8.9	4.2
5202-36-8	18	Cl	3.25	3.21	3.2	3.08	2.22	4.72	0.86	−0.59	−0.22	−2.23	−13.2	8.0	3.2
19095-29-5	20	OH	3.43	3.36	3.4	2.78	1.90	4.63	0.88	−0.29	0.10	−2.14	−12.6	7.4	2.4
19095-28-4	21	OCOMe	3.74	3.60	3.7	2.95	1.90	5.50	1.05	−0.46	0.10	−3.01	−13.3	7.6	2.5
40745-62-8	22	F[h]	3.92	3.76	3.9	2.85	2.11	5.31	0.74	−0.36	−0.11	−2.82	−13.3	7.19	1.82

[a] The data refer to 10% solutions in CS_2 unless otherwise indicated. Chemical shifts are believed to be significant to ±0.02 ppm and coupling constants to ±0.2 Hz. [b] See footnote *b*, Table I. [c] Dailey electronegativity. [d] Muller electronegativity. [e] Electronegativity value accepted in this work. [f] $J_{exo,exo} \cdot J_{endo,endo} = 9.16$ Hz (*cf.* text). [g] A. Dean and S. Sternhell, unpublished observations. [h] Data for 5 mol % solution in cyclohexane: S. L. Smith, University of Kentucky, private communication. [i] Reference 2.

TABLE III

NMR DATA FOR MONOSUBSTITUTED ETHYLENE OXIDES[a]



Registry no.	No.	X	E_X[b]			Chemical shifts, ppm (ex TMS)				Chemical shifts from parent (X = H), ppm			Coupling constants, Hz		
			c	d	e	H_A	H_B	H_C	$\delta_A - \delta_B$	H_A	H_B	H_C	J_{AB}	J_{AC}	J_{BC}
75-21-8	1	H	1.78	2.00	1.9	2.49 (2.54)[g]	2.49 (2.54)[g]	2.49 (2.54)[g]	0	0	0	0	−6.26 ± 1.6	4.43[f]	3.08[f]
75-56-9	3	Me[h]	2.07	2.23	2.1	2.59	2.28	2.85	0.31	−0.10	0.21	−0.36	5.37[f]	3.88[f]	2.57[f]
4538-51-6	8	CN[i]	2.49	2.58	2.5	3.12	3.00	3.50	0.12	−0.63	−0.51	−1.01	5.5	4.2	2.5
503-11-7	11	COOH[i]	2.60	2.68	2.6	2.99	2.93	3.48	0.06	−0.50	−0.44	−0.99	6.3	5.0	1.9
765-34-4		CHO[i]	2.69	2.75	2.7	3.17	3.10	3.35	0.07	−0.68	−0.61	−0.86	5.5	4.9	2.0
4401-11-0		$COCH_3$[j]	2.75	2.80	2.8	2.96	2.84	3.28	0.12	−0.47	−0.35	−0.79	5.7	4.3	2.7
96-09-3	12	Ph[i]	2.75	2.80	2.8	2.82	2.52	3.61	0.30	−0.33	−0.03	−1.12	5.7	4.0	2.5
7763-77-1	18	Cl[i]	3.25	3.21	3.2	2.83	2.75	4.90	0.08	−0.34	−0.26	−2.41	4.7	2.7	1.4
36099-39-5	21	OCOMe[i]	3.74	3.60	3.7	2.76	2.58	5.33	0.18	−0.27	−0.09	−2.84	4.5	2.2	1.4

[a] The data refer to 10% solutions in CS_2 unless otherwise indicated. Chemical shifts are believed to be significant to ±0.02 ppm and coupling constants to ±0.2 Hz. [b] See footnote *b*, Table I. [c] Dailey electronegativity. [d] Muller electronegativity. [e] Electronegativity value accepted in this work. [f] Probable error ≤0.01. [g] E. Lippert and H. Prigge, *Ber. Bunsenges. Ges.*, 67, 415 (1963). [h] Chemical shift data for CCl_4 solution [G. Allen, D. J. Blears, and K. H. Webb, *J. Chem. Soc.*, 810 (1965)]; coupling constants for neat liquid [D. D. Elleman, S. L. Manatt, and C. D. Pearce, *J. Chem. Phys.*, **42**, 650 (1965)]. [i] Reference 3. [j] Values for CCl_4 solution [J. L. Pierre, P. Chautemps, and P. Arnaud, *C. R. Acad. Sci.*, **261**, 4025 (1965)].

posed correlations[8] between geminal (J_{AB}) and vicinal (J_{AC} and J_{BC}) coupling constants in fragment 1 with electronegativity[9] and of the relative shielding of the β protons (H_A and H_B) by the substituent X. Scattered observations about the latter effect can be found in the literature[10a] and the substituents in this work were chosen to explore the effects of commonly encountered functional groups with the view of obtaining correlations useful in structural investigations.

Results and Discussion

The nmr data for acenaphthenes are presented in Table I, for hexachlorobicyclo[2.2.1]heptenes in Table II, for oxiranes in Table III, for 1,1-dichlorocyclopropanes in Table IV, and for dibenzobicyclo[2.2.2]octadienes in Table V. With the exception of the parameters for the parent hydrocarbons, most of the data in Tables II–V are taken from the literature and converted to units used to describe the acenaphthene series to allow direct comparison between the various series. Table VI gives nmr parameters for monosubstituted cyclopropanes abstracted from literature.[4,5,11] Entry numbers in each table refer to the same substituents.

A. Analysis of Nmr Spectra.—With the exception of entries 1–3 (Table I) the nmr spectra of 1-substituted acenaphthenes gave well-defined patterns for signals assigned to protons at C-1 and C-2. In all cases the relevant resonances were further split by coupling with aromatic protons[8] and analyses were performed on 100-MHz spectra with the latter decoupled. The spectra of 1-substituted acenaphthenes where the group X had

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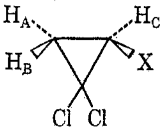
[9] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

[10] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969: (a) Chapter 3-8; (b) p 164; (c) Chapters 4-1 and 4-2; (d) p 64; (e) Chapter 2-2.

[11] R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967).

TABLE IV

NMR DATA FOR 2-SUBSTITUTED 1,1-DICHLOROCYCLOPROPANES[a]

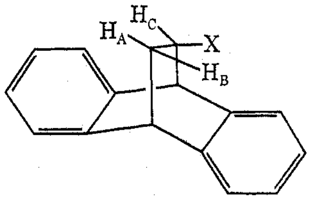


Registry no.	No.	X	E_X[b]			Chemical shifts, ppm (ex TMS)				Chemical shifts from parent (X = H), ppm			Coupling constants, Hz		
			c	d	e	H_A	H_B	H_C	$\delta_A - \delta_B$	H_A	H_B	H_C	J_{AB}	J_{AC}	J_{BC}
2088-35-9	1	H	1.78	2.00	1.9	1.45	1.45	1.45	0	0	0	0	−4.99[f] (−6.0)[g]	11.25[f] (11.2)[g]	7.99[f] (8.0)[g]
3591-38-6		$SiMe_3$	1.80	1.76	1.8	1.43	1.11	0.58	0.32	0.02	0.34	0.87	−4.9	12.6	9.6
5365-14-0	11	COOH[h]	2.60	2.68	2.6	1.87	2.02	2.52	−0.15	−0.42	−0.57	−1.07	−6.8	11.0	6.8
2415-80-7	12	Ph[h]	2.75	2.80	2.8	1.85	1.73	2.80	0.12	−0.40	−0.28	−1.35	−7.3	10.5	8.6
40745-72-0	14	Br[h]	2.96	3.10	3.0	2.08	1.58	3.45	0.50	−0.63	−0.13	−2.00	−8.6	9.4	6.6
17355-81-6	19	OMe[h]	3.30	3.25	3.3	1.67	1.52	3.62	0.15	−0.22	−0.07	−2.17	−8.4	7.9	5.3
3591-44-4	21	OCOMe[h]	3.74	3.60	3.7	1.84	1.58	4.28	0.26	−0.39	−0.13	−2.83	−9.1	8.0	5.4

[a] The data refer to 10% solutions in CS_2 unless otherwise indicated. Chemical shifts are believed to be significant to ±0.02 ppm and coupling constants to ±0.2 Hz. [b] See footnote *b*, Table I. [c] Dailey electronegativity. [d] Muller electronegativity. [e] Electronegativity value accepted in this work. [f] Probable error $\leqslant 0.03$. [g] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963). [h] Reference 3.

TABLE V

NMR DATA FOR 7-SUBSTITUTED DIBENZOBICYCLO[2.2.2]OCTADIENES[a]

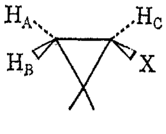


Registry no.	No.	X	E_X[b]			Chemical shifts, ppm (ex TMS)				Chemical shifts from parent (X = H) ppm			Coupling constants, Hz		
			c	d	e	H_A	H_B	H_C	$\delta_A - \delta_B$	H_A	H_B	H_C	J_{AB}	J_{AC}	J_{BC}
5675-64-9	1	H	1.78	2.00	1.9	1.68[f]	1.68[f]	1.68[f]	0	0	0	0	–	11.1 ± 0.1	4.4 ± 0.1
6372-65-2	13	NH_2[g]	2.91	2.93	2.9	2.14	0.97	3.11	1.17	−0.46	0.71	−1.43	−12.3	9.5	3.0
19371-69-8	16	$^+NMe_3{}^-Br$[h,i]	3.17	3.15	3.2	1.90	1.75	3.5	0.15	−0.22	−0.07	−1.8	−14.2	10.0	5.8
6476-45-5	18	Cl[g]	3.25	3.21	3.2	2.40	1.75	4.14	0.65	−0.72	−0.07	−2.46	−14.0	8.0	2.5
1521-59-1	20	OH[g]	3.43	3.36	3.4	2.19	1.18	3.94	1.01	−0.51	0.50	−2.26	−12.8	8.5	3.0
2975-83-9		OTs[g]	3.67	3.55	3.6	2.08	1.50	4.88	0.58	−0.40	0.18	−3.20	−13.8	9.0	3.5
1871-17-6	21	OCOMe[g]	3.74	3.60	3.7	2.25	1.41	4.90	0.84	−0.57	0.27	−3.22	−13.0	8.8	3.3

[a] Unless otherwise stated the data refer to CCl_4 solutions. Chemical shifts are significant to ±0.02 ppm and coupling constants to ±0.2 Hz. [b] See footnote *b*, Table I. [c] Dailey electronegativity. [d] Muller electronegativity. [e] Electronegativity value accepted in this work. [f] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964). [g] Reference 7. [h] Data for solution in CF_3COOH. [i] Y. Terui, K. Aono, and K. Tori, *J. Amer. Chem. Soc.*, **90**, 1069 (1968).

TABLE VI

NMR DATA FOR MONOSUBSTITUTED CYCLOPROPANES[a]



Registry no.	No.	X	E_X[b]			Chemical shifts, ppm				Chemical shifts from parent (X = H), ppm			Coupling constants, Hz		
			c	d	e	H_A	H_B	H_C	$\delta_A - \delta_B$	H_A	H_B	H_C	J_{AB}	J_{AC}	J_{BC}
75-19-4	1	H[f]	1.78	2.00	1.9	0.20	0.20	0.20	0	0	0	0	−4.34	8.97	5.58
594-11-6	3	Me[g]	2.07	2.23	2.2	0.40	−0.06	0.65	0.46	−0.20	0.26	−0.45	2.5	7.5	4.0
5500-21-0	8	CN[f]	2.49	2.58	2.5	0.94	0.94	1.36	0.00	−0.74	−0.74	−1.16	−4.72	8.43	5.12
1759-53-1	11	COOH[f]	2.60	2.68	2.6	0.91	1.01	1.59	−0.10	−0.71	−0.81	−1.39	−4.00	8.04	4.57
765-43-5		$COCH_3$[f]	2.75	2.80	2.8	0.81	0.85	1.96	−0.04	−0.61	−0.65	−1.76	−3.41	7.96	4.55
765-30-0	13	NH_2[f]	2.91	2.93	2.9	0.32	0.20	2.23	0.12	−0.12	0.00	−2.03	−4.29	6.63	3.55
4333-56-6	14	Br[f]	2.96	3.10	3.0	0.96	0.81	2.83	0.15	−0.76	−0.61	−2.63	−6.12	7.13	3.80
7393-45-5	18	Cl[f]	3.25	3.21	3.2	0.87	0.74	2.96	0.13	−0.67	−0.54	−2.76	−6.01	7.01	3.58
16545-68-9	20	OH[h]	3.43	3.36	3.4	0.59	0.34	3.35	0.25	−0.39	−0.14	−3.15	−5.43	6.19	2 94
1959-79-1	22	F[i]	3.92	3.76	3.9	0.69	0.27	4.32	0.42	−0.49	−0.07	−4.12	−6.69	5.89	2.39

[a] The data refer to neat liquids unless otherwise stated. [b] See footnote *b*, Table I. [c] Dailey electronegativity. [d] Muller electronegativity. [e] Electronegativity value accepted in this work. [f] Reference 4. [g] Data for chloroform solution [R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967)]. The data presented here were not used for plots of *J vs.* E_R etc., because of the unlikely value quoted for J_{gem} and lack of published details concerning the analysis of the nmr spectrum. [h] Data (ref 5) for 13 mol % solution in benzene. [i] Data (ref 5) for 8 mol % solution in 38 mol % benzene and 54 mol % trichlorofluoromethane.

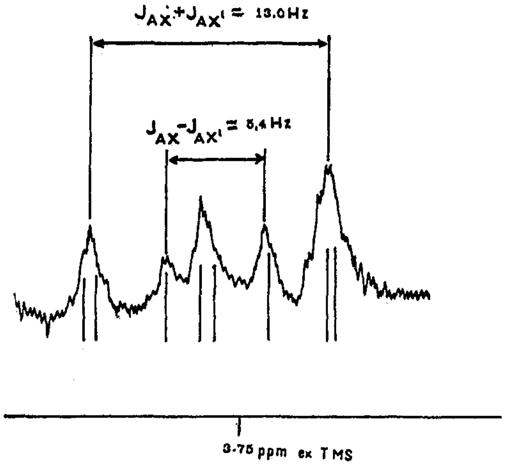


Figure 1.—Downfield ^{13}C satellite of the resonance assigned to benzylic protons in the 100-MHz spectrum of acenaphthene, with decoupling of the aromatic protons. The theoretical spectrum was generated (LAOCN3, stage I) for the AA'XX' system with $J_{AA'} = J_{XX'} = -18$, $J_{AX} = 9.2$, $J_{AX'} = 3.8$, and $\nu_{AX} = 64.5$ Hz (*i.e.*, $^1/_2J_{^{13}C,H}$), 10% w/v solution in CDCl$_3$.

protons coupled to H$_C$ (entries 4–7, Table I) were analyzed as ABX systems with coupling to protons in group X considered as first-order perturbations, which was justified by the $\Delta\nu/J$ ratios involved.

The nmr spectra of the remaining 1-substituted acenaphthenes (entries 8–21, Table I) were analyzed as ABC systems using the iterative computer program LAOCN3[12] executed on an IBM 7040/1401 in the Basser Computing Laboratory, School of Physics, University of Sydney. The errors quoted are probable errors appearing in the final iteration in the computer output.

Acenaphthene.—The ^{13}C satellites (Figure 1) of the resonance assigned to the benzylic protons were analyzed as an AA'XX' system with $\nu_{AX} = {}^1/_2J_{^{13}CH}$ by the method of Mortimer,[13] it being assumed that the signs of J_{AX} and $J_{AX'}$ are the same.[8] The experimental $J_{AX} + J_{AX'}$ and $J_{AX} - J_{AX'}$ values shown in Figure 1 are averages of five runs on each of the two satellites and are estimated to be significant to ±0.1 Hz. The theoretical AA'BB' spectrum shown in Figure 1 was generated with the LAOCN3 stage I (noniterative) program using the values for J_{AB} and $J_{AB'}$ obtained by measurement, $\nu_{AB} = {}^1/_2J_{^{13}CH}$ (64.5 Hz) and $J_{AA'}$ (= $J_{BB'}$) = -18 Hz. The appearance of the calculated spectrum is not sensitive to the magnitude of the last parameter.

1-*tert*-Butylacenaphthene.—The benzylic protons of *tert*-butylacenaphthene gave rise to a degenerate five-line pattern at 100 MHz, but, at 220 MHz, a well-resolved ABC spectrum[14a] which was analyzed with the aid of the LAOCN3 iterative program to give the parameters shown in Table I, entry 2.

1-Methylacenaphthene.—As the parameters of interest are the chemical shifts and coupling constants in the three-spin system at C-1 and C-2 (H$_A$, H$_B$, and H$_C$ in Table I), an attempt was made to simplify the 100-MHz nmr spectrum of 1-methylacenaphthene by decoupling both the methyl and aromatic protons. Unfortunately, at power levels required to decouple the methyl group, the portion of the spectrum of interest to us became distorted, while the portion of the spectrum comprising the six-spin system (H$_A$, H$_B$, H$_C$, and the methyl group), after the successful decoupling of aromatic protons, could not be analyzed because we were unable to obtain satisfactory initial parameters for the iterative stage. As homonuclear spin decoupling was not possible at 220 MHz, a specimen of 1-methyl-3,5,6,8-tetradeuterioacenaphthene was prepared (see Experimental Section), whose 220-MHz spectrum (Figure 2) was sufficiently simple to permit us to deduce trial parameters for analysis by means of the LAOCN3 procedure.[14b] Satisfactory analyses of both 220- and 100-MHz spectra were achieved, although the accuracy is rather poorer than usual owing to the large number of coincident transitions and imperfect resolution. The data for long-range interactions involving the methyl group are therefore of doubtful significance.

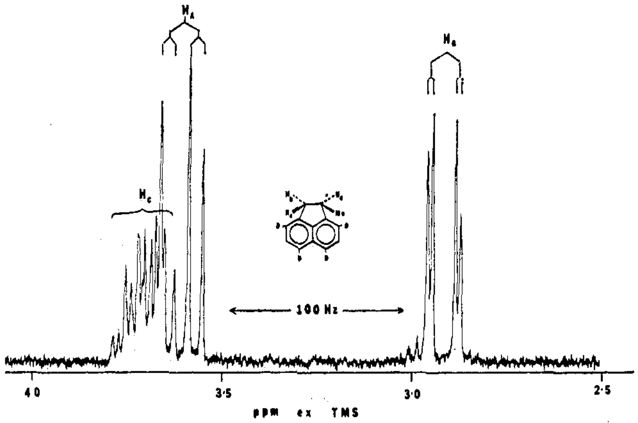


Figure 2.—Portion of 220-MHz spectrum of 1-methyl-3,5,6,8-tetradeuterioacenaphthene.

Hexachlorobicyclo[2.2.1]heptene.—The 100-MHz nmr spectrum of hexachlorobicyclo[2.2.1]heptene as approximately 10% w/v solution in CS$_2$ gave an AA'-BB' pattern with 24 clearly identifiable lines which was analyzed iteratively by LAOCN3 procedure to give the parameters listed under entry 1, Table II. The probable errors were all less than 0.02 Hz and the largest deviation between the experimental and calculated position of any single line was 0.106 Hz. The assignment of the upfield portion of the AA'BB' multiplet to the endo protons and the downfield portion to the exo protons was arrived at on the following grounds. It has been established[15,16] that in bicyclo[2.2.1]heptenes $J_{exo,exo}$ is somewhat larger than $J_{endo,endo}$ and, as $J_{AA'}$ and $J_{BB'}$ were available from the tightly coupled spectrum and differed significantly (9.16 and 9.73 Hz, respectively), a clear choice could be made. Secondly, comparison of the differences in the chemical shifts between H$_C$ and the parent compound in hexachlorobicyclo[2.2.1]heptenes (Table II) with the corresponding values for acenaphthenes (Table I) gave comparable values with the assignment chosen but some larger discrepancies for the alternative assignment. Finally, in norbornene[16] the resonances assigned to the analogous endo protons at C-5 and C-6 occur upfield of those assigned to the corresponding exo protons.

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(12) A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964), and private communication from the authors.

(13) F. S. Mortimer, *J. Mol. Spectrosc.*, **5**, 199 (1960).

(14) (a) Shown in microfilm edition. (b) A summary is given in the microfilm edition. See paragraph at end of paper regarding supplementary material.

(15) F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967), and references cited therein.

(16) A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968).

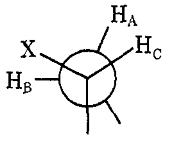
Ethylene Oxide and 1,1-Dichlorocyclopropane.—The nmr spectrum of ethylene oxide has been previously analyzed by the ^{13}C satellite method[13] as a neat liquid to give values ($J_{\text{cis}} = 4.45 \pm 0.1$ and $J_{\text{trans}} = 3.1 \pm 0.1$ Hz) almost identical with our results for CS_2 solution (entry 1, Table III) obtained by the iterative procedure.[12] The insensitivity of this spectrum to the magnitude of J_{gem} is reflected in the large probable error (±1.6 Hz) for this parameter in the final iteration where the root mean square (rms) error was 0.023 Hz and the largest deviation between the experimental and calculated line positions was 0.05 Hz.

The nmr spectrum of 1,1-dichlorocyclopropane in benzene has been analyzed by the ^{13}C satellite method.[17] Our results for CS_2 solution (entry 1, Table IV) are comparable. Owing to the relatively good quality of the satellite spectrum[18] and excellent convergence on iteration (rms error 0.013 Hz, largest deviation between the experimental and calculated line position 0.036 Hz), reliable results for all parameters, including J_{gem}, were obtained.

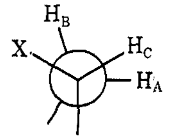
Dibenzobicyclo[2.2.2]octadiene gave a poor-quality ^{13}C satellite spectrum of the bridge protons after decoupling of the benzylic (bridgehead) protons.[19] Analysis by the method of Mortimer[13] was performed as for acenaphthene, using averages from eight spectra for the spacing assigned to the sum and difference, respectively, of the vicinal couplings.

B. Assignment of Resonances and Discussion of Geometry.—The resonances of the geminal protons at C-2 in 1-substituted acenaphthenes were assigned on the basis of the Karplus relation;[8] *i.e.*, it was assumed, following previous workers,[2–7] that in system **1** $J_{\text{cis}} > J_{\text{trans}}$. The same considerations were used to assign the coupling constants in the satellite analyses of the unsubstituted compounds (entries 1, Tables I–V).

No low-temperature neutron diffraction data on 1-monosubstituted acenaphthenes (**8**) are available and hence the central question of the exact stereochemistry of the system **1** in acenaphthene cannot be unequivocally answered. From the point of view of the present investigation, the most relevant distortions from the idealized stereochemistry of the system **1**, in which H_A is completely eclipsed by H_C and H_B is completely eclipsed by X, involve torsional changes about the C-1–C-2 bond. These are most likely to be of two kinds, represented by projections **9** and **10**. We consider that the most instructive of the available X-ray diffraction data on acenaphthenes[20–23] are those for *cis*-acenaphthene-1,2-diol,[21] which show that the analogous distortion from perfect eclipsing owing to the nonbonded interaction between the cis vicinal oxygen atoms is of the order of 10°. Consideration of van der Waals radii suggest that in the series of 1-substituted acenaphthenes examined here the most important nonbonded interactions, *i.e.*, those between H_B and X, are likely to be *less* severe (except possibly in cases 2, 15, and 16, Table I), and hence should result in distortions smaller than *ca.* 10°.



9



10

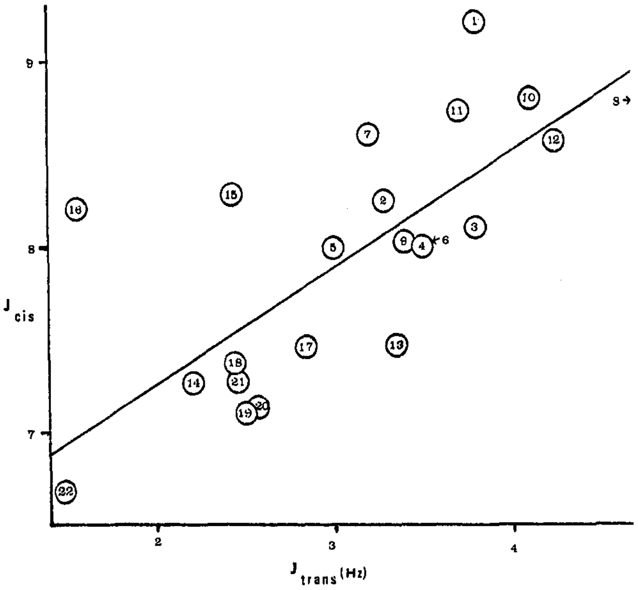


Figure 3.—Plot of $J_{\text{vicinal,cis}}$ (J_{AC}) *vs.* $J_{\text{vicinal,trans}}$ (J_{BC}) in 1-substituted acenaphthenes (**8**). Identification numbers refer to Table I. The straight line of best fit was obtained by the standard procedure and has slope 0.63, intercept on the y axis 6.00, and correlation coefficient 0.68.

Assuming, as is generally done,[8] that the most important factor determining the magnitude of vicinal coupling constants is the dihedral angle, one concludes that J_{trans} (*i.e.*, J_{BC}) in **8** should be more sensitive to distortions from perfect eclipsing than J_{cis} (*i.e.*, J_{AC}) because of the shape of the Karplus function.[8] The plot of J_{AC} *vs.* J_{BC} (Figure 3) shows considerable scatter, but there seems no unequivocal correlation between the bulk of substituent X and the deviation from the straight line of best fit, with the possible exception of 1-trimethylammonioacenaphthene (entry 16), thus suggesting that distortions are moderate.

It is apparent from the projections **9** and **10** that while distortion from perfect eclipsing must cause a decrease in J_{cis} it could be accompanied by either an increase (projection **9**) or a decrease (projection **10**) in J_{trans}. Comparison of pairs of entries in Table I where the substituents have similar electronegativity (see below) but differ in bulk leads to some very tentative suggestions. Thus the somewhat greater J_{trans} for X = Cl than for X = Br (in spite of an increase in electronegativity) suggests that the distortion (if any) is in the direction of projection **9**. On the other hand, entries 2 and 3 in Table I suggest that the *tert*-butyl group causes a distortion toward the projection **10**.

In summary, there is no evidence for *gross* distortions in monosubstituted acenaphthenes, but steric factors cannot be ignored.

C. Substituent Effects on Coupling Constants.—Previous workers[2–6,8,10c] have investigated the effect

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(17) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).

(18) Shown in microfilm edition.

(19) See microfilm edition.

(20) H. W. W. Ehrlich, *Acta Crystallogr.*, **10**, 699 (1957).

(21) J. Trotter and T. C. W. Mak, *ibid.*, **16**, 1032 (1963).

(22) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(23) (a) R. L. Avoyan and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **2**, 719 (1961); (b) *ibid.*, **4**, 631 (1963); (c) *ibid.*, **3**, 605 (1962); (d) T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, **16**, 811 (1963).

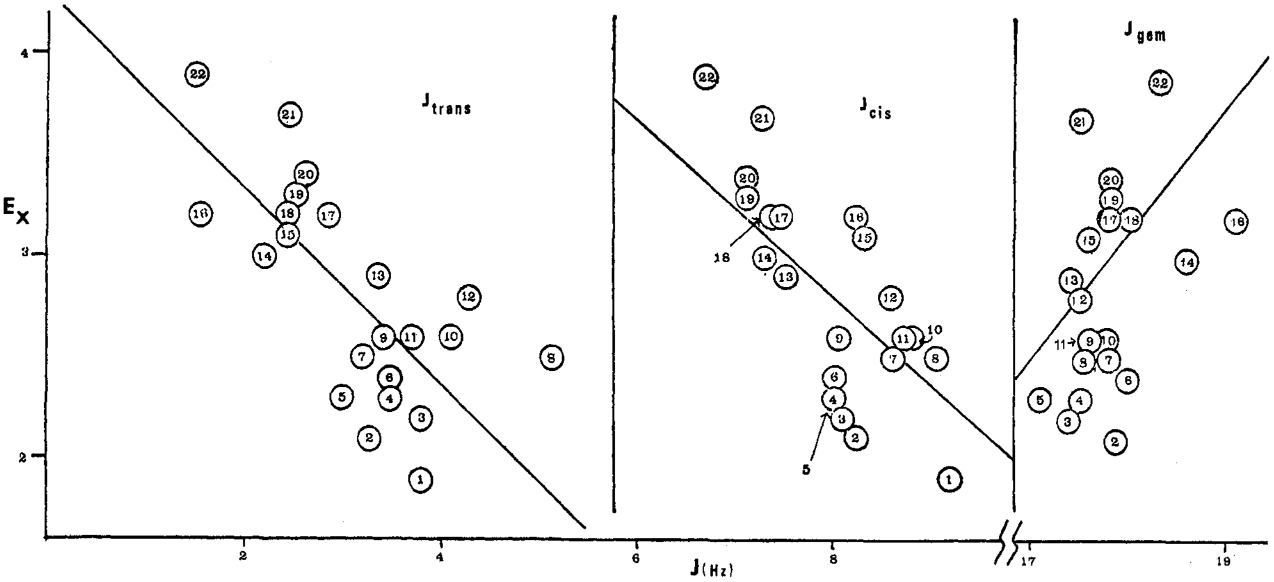

Figure 4.—Plot of coupling constants in 1-substituted acenaphthenes (8) *vs.* electronegativity of the substituents. Identification numbers refer to Table I. The straight lines of best fits were obtained by the standard procedure and have the following parameters: slope −0.48, −0.44, +0.42; intercept on the *y* axis 4.29, 6.32, −4.63; correlation coefficient −0.71, −0.74, 0.39 for J_{trans}, J_{cis}, and J_{gem}, respectively.

Table VII

Linear Correlation of Nmr Parameters with Electronegativity

System	Parameter	$\lvert J_{gem}\rvert$	J_{cis}	J_{trans}	$J_{cis} + J_{trans}$	$\delta_C - \delta_A$	$\delta_C - \delta_B$
Acenaphthene (Table I)	No. of points	21	22	22	22	21	21
	Slope	0.42	−0.44	−0.48	−0.31	0.59	0.53
	Intercept	−4.63	6.32	4.29	6.2	2.13	2.03
	Correlation coefficient	0.39	−0.72	−0.71	−0.79	0.93	0.91
Bicycloheptene (Table II)	No. of points	8	8	8	8	8	8
	Slope	1.51	−0.71	−0.49	−0.37	0.72	0.56
	Intercept	−16.3	8.9	4.7	7.3	2.0	1.8
	Correlation coefficient	0.83	−0.95	−0.84	−0.92	0.99	0.98
Oxirane (Table III)	No. of points	8	9	9	9	9	9
	Slope	−0.55	−0.40	−0.81	−0.35	0.50	0.50
	Intercept	5.8	4.3	4.5	4.9	2.3	2.2
	Correlation coefficient	−0.68	−0.67	−0.87	−0.82	0.88	0.83
Dichlorocyclopropane (Table IV)	No. of points	7	7	7	7	7	7
	Slope	0.41	−0.40	−0.39	−0.26	0.55	0.57
	Intercept	−0.2	6.7	5.6	7.2	2.2	2.1
	Correlation coefficient	0.97	−0.94	−0.86	−0.94	0.98	0.98
Dibenzobicyclooctadiene (Table V)	No. of points	6	7	7	7	7	7
	Slope	0.11	−0.60	−0.17	−0.17	0.58	0.49
	Intercept	1.8	8.8	3.7	5.3	2.1	2.0
	Correlation coefficient	−0.2	−0.76	−0.28	−0.56	0.96	0.95
Cyclopropane (Table VI)	No. of points	9	9	9	9	9	9
	Slope	0.32	−0.57	−0.56	−0.25	0.48	0.46
	Intercept	1.3	7.1	5.1	5.8	2.13	2.11
	Correlation coefficient	0.71	−0.99	−0.94	−0.95	0.97	0.97

of electronegativity on vicinal and geminal coupling constants in many systems and found definite correlations. Plotting the relevant data from Table I against the mean of Dailey[9] and Muller[24] electronegativities (Figure 4) confirms the general *trends* noted previously, but clearly it is futile to propose any definite correlations in view of the degree of scatter.

Besides the apparent lack of a simple relation between electronegativity and coupling constants shown in Figure 4, a number of significant particular exceptions to any proposed relation of type $J = EA + B$, where A and B are constants, can be seen in Tables I–VI. Thus the vicinal coupling constants in 1-cyanoacenaphthene (entry 8, Table I) are abnormally large, although this is not observed in the cyano derivatives of hexachlorobicyclo[2.2.1]heptene (entry 8, Table II),

[24] J. C. Muller, *Bull. Soc. Chim. Fr.*, 1815 (1964).

TABLE VIII

DIRECT COMPARISON BETWEEN COUPLING CONSTANTS

System	Parameter	$\lvert J_{gem} \rvert$	J_{cis}	J_{trans}	$J_{cis} + J_{trans}$
Bicycloheptene *vs.* acenaphthene	No. of points	7	8	8	8
	Slope	1.22	0.70	1.23	0.88
	Intercept	1.99	2.2	−1.04	1.8
	Correlation coefficient	0.54	0.97	0.93	0.98
Oxirane *vs.* acenaphthene	No. of points	6	7	7	7
	Slope	0.0	0.72	1.05	1.01
	Intercept	17.6	5.6	1.33	5.97
	Correlation coefficient	−0.04	0.90	0.73	0.90
Dichlorocyclopropane *vs.* acenaphthene	No. of points	5	6	6	6
	Slope		0.63	0.52	0.68
	Intercept		1.9	−0.40	0.00
	Correlation coefficient		0.95	0.84	0.93
Dibenzobicyclooctadiene *vs.* acenaphthene	No. of points	5	6	6	6
	Slope		0.42	−0.20	0.34
	Intercept		3.87	3.45	6.65
	Correlation coefficient		0.91	−0.32	0.55
Cyclopropane *vs.* acenaphthene	No. of points	7	8	8	8
	Slope	0.58	0.75	0.86	1.01
	Intercept	14.8	2.39	−0.30	0.10
	Correlation coefficient	0.88	0.97	0.84	0.91
Cycloheptene *vs.* cyclopropane	No. of points	6	6	6	6
	Slope	1.94	1.21	1.00	1.24
	Intercept	−19.6	−2.7	0.66	−3.05
	Correlation coefficient	0.89	0.95	0.90	0.98
Cycloheptene *vs.* oxirane	No. of points	5	6	6	6
	Slope		0.23	0.56	1.20
	Intercept		1.76	0.01	−8.8
	Correlation coefficient		0.74	0.62	0.98

ethylene oxide (entry 8, Table III), or cyclopropane (entry 8, Table VI).[25] Geminal coupling constants for all bromo derivatives (entries 14 in Tables I, IV, and VI) are too small (large negative values) and several other prominent irregularities of the same type can be discerned in Tables I–VI.

Replotting data from Tables I–VI in the manner shown in Figure 4 shows (Table VII) that the degree of correlation varies significantly but, owing to the small number of derivatives in several series, it is difficult to draw any firm conclusions. There does not appear to be any clear relation between the size of X and deviation from straight-line relationships, and hence steric factors are unlikely to be solely responsible for the poor and variable correlation between E_X and coupling constants in system **1**.

We conclude that, within the comparatively narrow range of electronegativity values associated with commonly encountered functional groups, correlations between vicinal and geminal coupling constants and electronegativities of functional groups are of doubtful significance. It can be seen (Figure 4) that the scatter for J_{trans} is not much greater than that for J_{cis} and, by arguments advanced above, this confirms that the poor correlation with electronegativity is not solely due to steric factors. It is more likely that the "Dailey-type" measures of electronegativity[10d] are not very meaningful for narrow ranges found among common functional groups. In view of this and the uncertain status[26] of the underlying theory, we feel that, for the purpose of structural determination, it would be more useful to look for regularities in the influence of substituents on the magnitude of coupling constants rather than for the influence of a general property of substituents, such as electronegativity.

Comparisons of data for different systems (Tables I–VI) suggests that in the generalized system **1** substituents are indeed associated with characteristic values of vicinal coupling constants. Thus plots of the sums[27] of vicinal coupling constants in acenaphthenes *vs.* hexachlorobicyclo[2.2.1]heptenes (Figure 5) and cyclopropanes (Figure 6) appear to be straight lines.

Clearly the data in Tables I–VI could give rise to a very large number of plots of the type shown in Figures 5 and 6. These were chosen as illustrations because of the relatively large number of data available. While other plots appear less convincing, they show considerably more correlation between the substituent effects in different systems than between the sums of vicinal coupling constants and "electronegativity" in each system (Tables VII and VIII). The existence of sub-

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[25] We are excluding the entry for methylcyclopropane[11] (entry 3, Table VI) because of the unlikely value quoted for J_{gem} and lack of published details concerning the analysis of the nmr spectrum.

[26] T. Schaefer and H. M. Hutton, *Can. J. Chem.*, **45**, 3153 (1967).

[27] The sums of the vicinal coupling constants were chosen because they are least susceptible to errors in analyses.

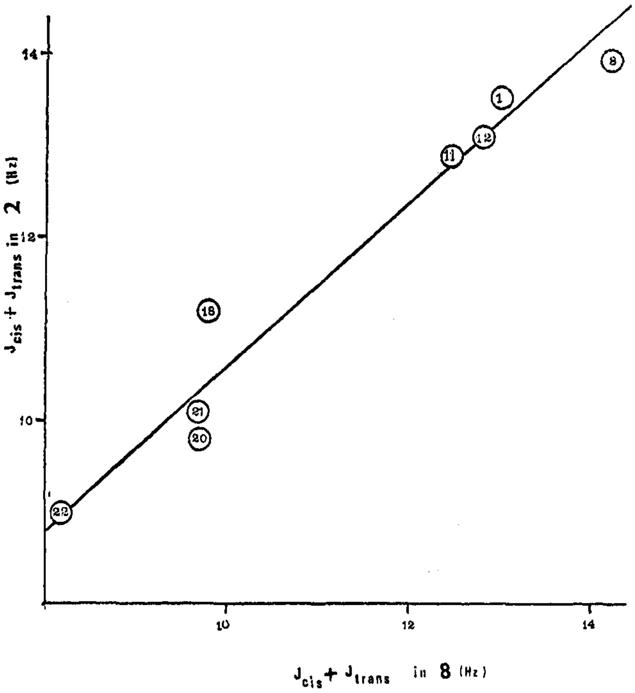

Figure 5.—Plot of the sums of vicinal coupling constants in monosubstituted hexachlorobicyclo[2.2.1]heptenes (**2**) *vs.* the sums of vicinal coupling constants in 1-substituted acenaphthenes (**8**). Identification numbers refer to Tables I and II. The straight line of best fit was obtained by the standard procedure and has slope 0.88, intercept on the *y* axis 1.8, and correlation coefficient 0.98.

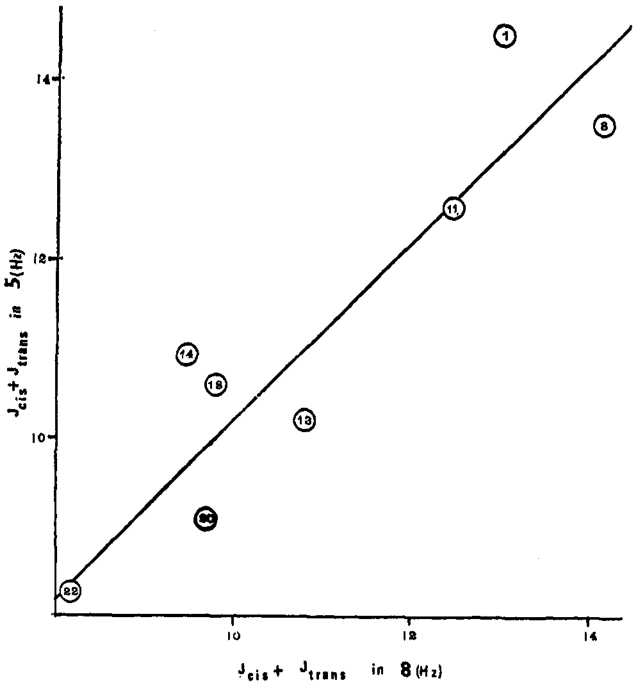

Figure 6.—Plot of the sums of vicinal coupling constants in monosubstituted cyclopropanes (**5**) *vs.* the sums of vicinal coupling constants in 1-substituted acenaphthenes (**8**). Identification numbers refer to Tables I and VI. The straight line of best fit was obtained by standard procedure and has slope 1.01, intercept on the *y* axis −0.10, and correlation coefficient 0.91.

stituent effects of this type has obvious predictive value for structural work.

D. Substituent Effects on Chemical Shifts.—The causes of some substituent effects on chemical shifts in system **1** will be discussed below; in this section we are concerned with establishing the *regularity,* if any, in substituent influences in this system for the purpose of obtaining correlations useful in structural determination.

It is well known[28] that the minimum experimental conditions for obtaining genuinely meaningful chemical shift data consist of extrapolation to infinite dilution in a completely inert, isotropic solvent using suitable internal standards. Such conditions must conflict with even the most painstaking routine operations because spectral analysis on very dilute solutions becomes virtually impossible, owing to unfavorable signal to noise ratio, and because the solubility of the majority of organic compounds in "inert isotropic solvents" is inadequate.[29] As the principal purpose of this work was to establish correlations usable in structural determinations, the nmr spectra of the series of 1-substituted acenaphthenes **8** were determined in deuteriochloroform solutions. For a number of compounds (Table I) it was also possible to obtain spectra for dilute (1–3%) solutions in carbon tetrachloride. It can be seen that, although the actual chemical shifts in the two solvent systems vary quite appreciably (up to 0.13 ppm), the internal chemical shifts vary considerably less and it is the latter which are most likely to be useful in the present context.

Several investigators[2–6] have commented about the good correlation between electronegativity and the internal chemical shifts in systems incorporating the fragment **1**, and analogous plots for 1-substituted acenaphthenes (Figure 7) are indeed straight lines. This indicates that solvent effects are unlikely to be a major influence.[32] We consider, however, that plots of this nature are of little direct significance to the problem of the relation between shielding and electronegativity in complex molecules, because the electronegativity values of "Dailey type" [9,24] are linear functions of analogous internal chemical shifts in the corresponding ethyl derivatives CH_3CH_2X. In other words, plots of the type shown in Figure 7 are plots of $\delta_{H_\alpha} - \delta_{H_\beta}$ in two systems $CH_\beta CH_\alpha X$ differing only in stereochemistry.

Data in Tables I–VI reveal that all substituents, with the exception of $-SiMe_3$ in all systems[33] investigated here, deshield the geminal proton (H_C) and the trans vicinal proton (H_A) with respect to the parent compound (X = H), but the eclipsed cis vicinal proton (H_B) generally experiences smaller relative downfield shifts and in several cases is actually shielded. Not surprisingly, with most substituents the eclipsed vicinal proton appears upfield of the trans vicinal proton, *i.e.*, the values in the column $\delta_A - \delta_B$ are generally positive. Carbonyl derivatives (X = COOH, $-COOMe$, $-CO$-

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[28] P. Laszlo in "Progress in NMR Spectroscopy," Vol. 3, Pergamon Press, Elmsford, N. Y., 1967, Chapter 6.

[29] It has been shown recently[30] that even carbon tetrachloride, which has been almost universally used as an "inert isotropic solvent" in nmr spectroscopy, is not always reliable, while the ubiquitous deuteriochloroform is known[31] to cause quite large solvent shifts.

[30] T. Schaefer, B. Richardson, and R. Schwenk, *Can. J. Chem.,* **46,** 2775 (1968).

[31] P. Laszlo, *Bull. Soc. Chim. Fr.,* 2658 (1964).

[32] R. F. Zürcher in "Progress in NMR Spectroscopy," Vol. 2, Pergamon Press, Elmsford, N. Y., 1967, Chapter 5.

[33] Data for hexachlorobicyclo[2.2.1]heptenes (Table II) can be compared with those for the remaining systems only after correcting for the inherent differences in chemical shifts between H_A and H_B (0.49 ppm), which involves making the unverifiable assumption that this factor remains constant throughout the series.

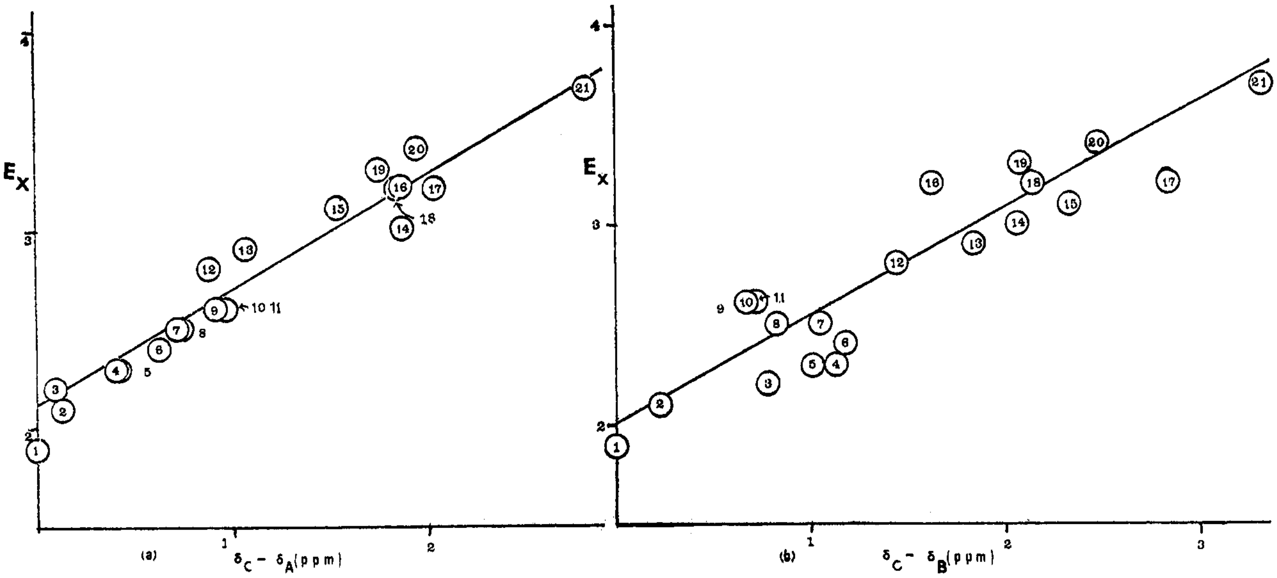

Figure 7.—Plots of the internal chemical shifts in 1-substituted acenaphthenes (**8**) *vs.* electronegativity of the substituent: (a) for the proton trans to the substituent (H_A); (b) for the proton cis to the substituent (H_B). Identification numbers refer to Table I. The straight lines of best fit were obtained by standard procedure and have the following parameters: slope 0.59, 0.53; intercept on *y* axis 2.13, 2.03; correlation coefficient, 0.93, 0.91 for plots 10a and 10b, respectively.

NH_2, -COMe, and -CHO) show either the opposite or erratic behavior, which can be readily rationalized by taking into account the variable conformation of the highly anisotropic carbonyl group. In the acenaphthene series (Table I, entry 16) but not in the dibenzobicyclo[2.2.2]octadiene series (Table V, entry 16), the trimethylammonium group also gives a negative value for $\delta_A - \delta_B$.

Clearly caution is necessary in utilizing the "eclipsed upfield" rule, particularly where the substituent lacks axial symmetry about the C–X bond, but it is capable of giving structural information.[10a,34] The effect of the methyl group has been established independently.[35]

Comparing the values of $\delta_A - \delta_B$ in Tables I–VI for substituents where conformational factors can be neglected (*i.e.*, here for X = Me, *tert*-butyl, CN, Br, Cl, and F) shows that the magnitude of the effect varies considerably without showing any obvious trends for the limited data available. It is therefore important that for structural determinations, an appropriate model should be chosen.

E. Rationalization of Some Substituent Effects in Fragment 1.—Because of the inherent difficulties in theoretically estimating chemical shifts, the main aim of this work has been to provide empirical parameters for common substituent effects which may be transferred from one system to another. However, a number of insights into the factors which contribute to substituent-induced chemical shifts may be gained from a collection of selected data from Tables I–VI. For ease of interpretation, the substituents to be examined have been restricted to substituents where the X in the C–X bond is a first-row element. In addition highly anisotropic groups such as carbonyl containing substituents have been given minimal consideration. Even with these limitations, no general, highly accurate correlations can be made which can account for all of the observed chemical shifts. Thus the estimation of substituent chemical shifts must remain empirically based. However, within the limitations specified by the selection of data, some trends are detected which may prove generally useful and should serve as the basis for future investigations.

The possible contributing factors which generate substituent chemical shifts have been discussed in detail by many authors.[10e,32] The diamagnetic screening term is the dominant effect on proton chemical shifts and it is directly proportional to the electron density at the proton in question. While this fact has been recognized for many years, the analysis of the electron density changes in terms of the various contributing factors (inductive effect, electric field effects, etc.) has remained uncertain. When chemical shift variations in substituted alkanes of 0.3 ppm or less are being considered, any or all of the possible contributors (diamagnetic shielding, short-range paramagnetic interaction, neighboring group anisotropy, solvent effects, and intermolecular interactions) may provide a rationalization. Larger changes can only be accounted for by the diamagnetic screening term or less commonly by the neighbor anisotropy term when a highly anisotropic group is involved.

The most readily apparent chemical shift change with substitution occurs at the geminal (α) proton. Many authors have provided electronegativity correlations to account for this behavior, but deviations from these simple correlations are well known. The definitive studies by Cavanaugh and Dailey[9] and Spiesecke and Schneider[36] provided a basis for subsequent studies.

The X substituents for system 1 can be arranged in order of increasing downfield shift and this ordering correlates moderately well with the electronegativity of X (of Tables I–VI and Figure 7). There are a few *minor* inversions from substrate to substrate, but these are found with groups which have large magnetic anisotropies (*e.g.*, C=O) or the substituent to carbon

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[34] C. J. Moye and S. Sternhell, *Aust. J. Chem.*, **19**, 2107 (1966); R. H. Andreatta, V. Nair, and A. V. Robertson, *ibid.*, **20**, 2701 (1967).

[35] E. Pretsch and W. Simon, *Helv. Chim. Acta*, **52**, 2133 (1969).

[36] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

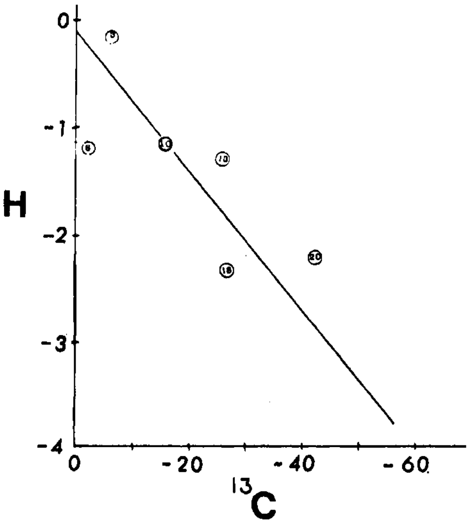

Figure 8.—Plot of α-proton shift of substituted acenaphthenes *vs.* ^{13}C substituent effect (from ref 38). Similar plots are obtained for methyl, ethyl, and cyclopropyl derivatives (see Table X). Substituents are labeled according to Table I.

bond involves a non-first-row element (*e.g.*, Br·). This substituent sequence holds not only for systems **2**–**8** but also for methyl, ethyl,[10] adamantyl,[37] and vinyl compounds.[10] Furthermore it correlates well with the ^{13}C chemical shifts of the carbons in the C–X group of simple alkanes.[38]

In addition to the substituent dependence, a careful examination reveals that the influence of a given substituent depends on the substrate in question. This dependence is illustrated by the substituent chemical shifts of protons α to an OH (relative to the corresponding hydrocarbon): methyl (3.16), cyclopropyl (3.15), ethyl (2.73), isopropyl (2.61), system **7** (2.26), system **8** (2.23), system **2** (2.14), 2-adamantyl (2.02), vinyl (1.22). A similar order of substrates is shown with other electronegative substituents.

The substrate dependence can be put on a quantitative basis by plotting the α-proton shift against a standard ^{13}C substituent chemical shift (Figure 8). Although this plot is clearly not a linear function—proton shifts change more slowly than carbon shifts—a least squares treatment can be used to provide an approximate measure of substrate sensitivity. The available results are given in Table IX. There is insufficient data for other substrates to provide a meaningful plot. The cyano group invariably falls off the correlation line and this can be attributed to a low value for the carbon shift of the carbon α to cyano. The apparently anomalous position of the acenaphthyl substrate is readily understood when it is realized that the data for fluoride as a substituent were not available. Thus the approximation of a curved line by a straight line will fail. This emphasizes the need for a wide range of data if a measurement of substrate sensitivity is to be made. A knowledge of substrate sensitivity will be useful for chemical shift predictions because a relationship akin to the classical Hammett $\sigma\rho$ treatment can be applied. Because of the limitations set by compound and data availability, the following relationship (eq 1) is suggested for chemical shift estimation,

$$\Delta\delta_{\mathrm{RX}} = \Delta\delta_{\mathrm{EtX}};\ \Delta\delta_{\mathrm{ROH}}/\Delta\delta_{\mathrm{EtOH}} \qquad (1)$$

where $\Delta\delta$ represents the substituent chemical shift of the α proton relative to the corresponding hydrocarbon RH. Of course other common substituents besides OH could be used, provided that the magnitude of $\Delta\delta$ is large enough to provide a reliable ratio. If a sufficiently wide range of substituents is available, it would be preferable to use an analysis based on Table IX. The results for estimating acenaphthene shifts with the equation above are shown in Table X. It is clear that major discrepancies arise with the highly anisotropic *N*-acetyl and *O*-acetyl substituents and this serves as a warning that highly anisotropic groups should be treated with caution.

The combination of substituent and substrate dependence of chemical shifts of α protons clearly supports the long-held view that the diamagnetic screening term is dominant in controlling proton chemical shifts. In particular the magnetic anisotropy of the C–X bond cannot contribute significantly to the observed α-proton shift. This term should be essentially independent of substrate given the limited geometry available for an H–C–X group. Only a change in H–C–X bond angle should alter this term significantly and there is no correlation between bond angle and substrate sensitivity. The results for the methyl and cyclopropyl

Table IX

Substrate Sensitivity to Substituent[a] (Correlation of Proton Chemical Shifts with Carbon Chemical Shifts)

Substituent	Slope (m)	Intercept (c)	Correlation coefficient
Cyclopropyl	0.060	−0.58	0.94
Methyl	0.054	−0.90	0.92
Ethyl	0.049	−0.75	0.90
Acenaphthenyl[b]	0.065	−0.10	0.86
Vinyl	0.019	−0.30	0.82

[a] Data for plot of substituent-induced α-proton shift (δ_{H}) against ^{13}C substituent shift ($\delta_{^{13}\mathrm{CX}}$). $\delta_{\mathrm{H}} = m\ \delta_{^{13}\mathrm{CX}} + c$. Note that the ^{13}C data is for simple alkanes from ref 38. [b] This correlation does not include the fluoro derivative; see text.

Table X

Comparison of Observed[a] and Predicted Chemical Shifts of Acenaphthene Derivatives Based on Equation 1

X	Calcd	Obsd	Calcd − obsd
Me	−0.04	−0.17	0.13
CH_2COMe	−0.55	−0.71	0.16
CH_2COOH	−0.65	−0.75	0.10
CN	−1.17	−1.19	0.02
$CONH_2$	−1.08	−1.03	−0.05
COOMe	−1.12	−1.13	0.01
COOH	−1.18	−1.19	0.01
Ph	−1.39	−1.35	−0.04
NH_2	−1.48	−1.35	−0.13
Br	−1.98	−2.35	0.37
$NHCOCH_3$	−1.85	−2.56	0.71
Cl	−2.06	−2.31	0.25
OMe	−1.98	−2.03	0.05
OH	−2.15	−2.23	0.08
OCOMe	−2.51	−3.14	0.63
F	−2.76		

[a] The values for EtOH and EtX are taken from ref 10.

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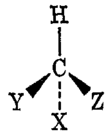
(37) R. C. Fort and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

(38) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley, New York, N. Y., 1972, pp 47, 48.

compounds are particularly informative here, because these groups of compounds should show the largest variation in bond angle, but their sensitivities to a given substituent are very similar. In addition, the close correlation between proton and carbon shifts further supports this conclusion because the magnetic anisotropy contribution would be expected to be substantially different for carbon and hydrogen. Their geometric orientation with respect to the anisotropic group and the substantial difference in their gyromagnetic ratios should lead to quite different anisotropy contributions.



The ordering of substrates is readily explicable in terms of an inductive effect model. Consider the molecular fragment shown in the structure, where X is an electronegative substituent which withdraws electrons from carbon (relative to H as a substituent). The carbon in turn withdraws electrons from the C–H, C–Y, and C–Z bonds. If one of the substituents Y or Z is a more electron-rich element or has a more polarizable bond (*i.e.*, any of the substrates studied here), then the inductive effect of the X group will be compensated predominantly by the C–Y group rather than the C–H group. Thus, of all the substrates available, the methyl group should show greatest substituent sensitivity. In the other systems, Y and Z are carbon atoms and the substrate sensitivity reflects the ability of the carbon framework to replace the electrons withdrawn by X. The more readily the carbon framework can provide electrons the less demand there is on hydrogen and so the lower the substrate sensitivity. In the strained cyclopropyl system, inductive electron withdrawal by X would weaken the C–C bonds, a highly unfavorable process, and thus major compensation is provided by the C–H bond and a large substrate sensitivity results. Simple alkyl compounds show a lower sensitivity, followed by the electron-rich systems **2**, **7**, and **8** and finally the readily polarizable vinyl group. The position of the adamantyl group as a low-sensitivity framework is interesting and suggests the intriguing possibility that the number of β carbon–carbon bonds is an important factor in governing substrate sensitivity. This is consistent with the inductive model, as β carbon–carbon bonds will be better able to compensate for electron removal from the β carbon than β carbon–hydrogen bonds.

The interpretation of the vicinal (β) hydrogen shifts H_A and H_B is complex. The magnitude of the observed shifts is sufficiently small that any or all of the factors which control chemical shifts could make a significant contribution. In a rigid system, the different orientation of H_A and H_B to the substituent X provides a limited probe for separation of these contributions. Zürcher[32] has given a thorough review of the necessary relationships. Since the shift of the α proton (H_C) is dominated by the inductive effect, a plot of H_C *vs.* H_A or H_B should show the importance of inductive effects. Using all the acenaphthene data, a mild trend of H_A to follow H_C was shown (correlation coefficient 0.69) and the eclipsed proton H_B showed no correlation. Thus the inductive effect does not dominate β-proton shifts. Some of the data spread may be attributed to the effect of anisotropic groups of unknown conformation. However, even when the data is limited to axially symmetrical substituents no general trends were apparent. An attempt was made to predict some of these shifts using Zürcher's parameters[32] for electric field and anisotropy contributions, but this also failed (Table XI).

In an attempt to overcome some of the deficiencies of the point dipole approximation an alternative representation was tried. The C–X bond electric field was approximated by point charges at the nuclei and a Buckingham[39] electric field calculation was performed. The magnitudes of the nuclear charges were chosen so as to reproduce the dipole moment in conjunction with the C–X bond length. The resultant electric field was calculated at the center of the C–H bond in question. The chemical shifts calculated by this method were usually within about 0.1 ppm of the simple point dipole values and so offer no advantages.

Thus there is no simple single correlation which will account for β-proton shifts. However, it is apparent that for simple substituents (Me, NH_2, OH, F), the electrical character of the X substituent does have a marked influence on the shifts of H_A and H_B (Figure 9). The breakdown of this behavior into the contributions due to through-bond and through-space effects must await further data.

The major stumbling block in all these calculations is the upfield shift induced at the eclipsed hydrogen. As Zürcher has shown,[32] none of the normal electric field or anisotropy contributions can reproduce this behavior. Zürcher interpreted the results as a solvent effect, but this effect has since been shown to be insufficient by the work of Simon[35] among others. Since none of the recognized factors controlling chemical shift can account for the observed behavior, it seems that some previously undetected effect must be invoked.

Whatever this mechanism is, it must be strongly geometry dependent. Furthermore, it would seem from Figure 9 that the factor responsible for the upfield shift is approximately constant for each substituent. Since it is most unlikely that a completely new electromagnetic phenomenon is responsible for this behavior, it seems reasonable to suggest that a neglected component in the diamagnetic shielding term is responsible. The strong dependence on dihedral angle (0.7 ppm at 0°, 0.4 ppm at 60°, 0 at 120°) (Figure 10) and the approximate independence to the substituent are strongly reminiscent of the Karplus relationship for vicinal coupling constants.[40] This suggests that the explanation lies in a small amount of backbonding from the substituent to the eclipsed hydrogen. This will increase the electron density at the proton and generate an upfield shift. Unfortunately, no reliable data are available for a dihedral angle of 180° and so determination of the total shape of the backbonding contribution must await further experiments.

Experimental Section

Melting points were obtained on a Kofler block and are uncorrected. Ir spectra were determined with a Perkin-Elmer Model

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(39) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(40) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

TABLE XI

OBSERVED AND CALCULATED RELATIVE PROTON CHEMICAL SHIFTS OF THE RIGID SYSTEM XC–CH FOR DIFFERENT SUBSTITUENTS X AND TORSION ANGLES ϕ

System	Torsion angle ϕ	$-\Delta\delta_{\text{obsd}}$,[a] ppm	κ[b]	$\Delta\chi_1$[c]	$-\Delta\delta_{\text{el}}$, ppm	$-\Delta\delta_{\text{magn}}$, ppm	$-\Delta\delta_{\text{calcd}}$,[d] ppm	$-\Delta\delta_{\text{obsd}} - \Delta\delta_{\text{calcd}}$, ppm
Chloro Compounds[e]								
8	0	0.16	−9.0	0	0.83	0	0.83	0.67
			−5.7[h]	−7.5	0.52	0.06	0.58	0.42
	128	0.46	−9.0	0	0.26	0	0.26	−0.20
			−5.7[h]	−7.5	0.16	0.02	0.18	−0.28
2	0	0.22	−9.0	0	0.88	0	0.88	0.66
			−9.0	−7.5	0.88	0.05	0.93	0.71
	120	0.59	−9.0	0	0.50	0	0.50	−0.09
4	0	0.26	−9.0	−7.5	0.49	−0.11	0.38	0.13
	144[o]	0.34	−9.0	−7.5	<0.22	−0.05	<0.17	−0.17
7	0	0.07	−9.0	−7.5	0.80	0.07	0.87	0.80
	120	0.72	−9.0	−7.5	0.51	0.02	0.53	−0.19
5	0	0.54	−9.0	−7.5	0.51	−0.15	0.34	0.20
			−5.7	0	0.34	0	0.34	0.20
	144	0.67	−9.0	−7.5	<0.22	0.05	<0.17	−0.49
Bromo Compounds[f]								
8	0	0.29	−9.4[i]	−10[p]	0.84	0.08	0.92	0.63
			−6.0[j]	−10	0.53	0.08	0.61	0.32
	128	0.48	−9.4	−10	0.27	0.03	0.30	−0.18
			−6.0	−10	0.16	0.03	0.19	−0.29
3	0	0.61	−9.4	−10	0.50	−0.15	0.45	−0.17
	144	0.76	−9.4	−10	<0.25	−0.06	<0.19	−0.57
Cyano Compounds[g]								
8	0	0.36	−14.8[p]	−30[k]	0.41	−0.19	0.22	−0.14
			−14.8	0	0.41	0	0.41	0.05
	128	0.46	−14.8	0	0.16	0	0.16	−0.30
2	0	0.15	−14.8	0	0.50	0	0.50	0.35
	120	0.21	−14.8	0	0.36	0	0.36	0.15
4	0	0.51	−14.8	−30	0.33	−0.20	0.13	−0.38
			−14.8	0	0.33	0	0.33	−0.18
	144	0.63	−14.8	0	<0.15	0	<0.15	−0.48
Methyl Compounds								
8	0	−0.62	0	*l*	0	−0.57[n]	−0.57	0.05
				m	0	−0.37[n]	−0.37	0.25
	128	0.09	0	*l*	0	0.01	0.01	−0.08
				m	0	0.06	0.06	−0.03

[a] See Tables I–VI. [b] $\times 10^{-12}$ esu. [c] $\times 10^{-30}$ cm^3/molecule. [d] $\Delta\delta_{\text{calcd}} = \Delta\delta_{\text{el}} + \Delta\delta_{\text{magn}}$. [e] Center of dipole from carbon atom = 0.90 Å (ref 32). [f] Center of dipole from carbon atom = 0.96 Å. [g] Center of dipole from carbon atom = 2.1 Å (ref 32). [h] $A = -2.6 \times 10^{-12}$ esu and μ(C–Cl) = 2.2 D. [i] $A = -4.07 \times 10^{-12}$ esu and μ(C–Br) = 2.3 D. [j] $A = -2.6 \times 10^{-12}$ esu and μ(C–Br) = 2.3 D. [k] Mean of values determined by W. Zeil and H. Buchert, *Z. Phys. Chem.*, **38,** 47 (1963), and G. S. Reddy and J. H. Goldstein, *J. Phys. Chem.*, **39,** 3509 (1963). [l] $\Delta\chi_{\text{C–C}} = 21.33$ and $\Delta\chi_{\text{C–H}} = 12.57$. [m] $\Delta\chi_{\text{C–C}} = 13.98$ and $\Delta\chi_{\text{C–H}} = 11.00$. [n] Calculated for H–C–C and C–C–CH_3 angles of 109°. Corresponding angles in acenaphthene are 119°. [o] Reference 3. [p] Reference 32.

221 spectrophotometer. Nmr spectra were obtained on a Varian Associates Model A-60 or HA-100 spectrometer using tetramethylsilane, unless otherwise indicated, as internal reference. Some of the spectra were recorded with a Varian HR-220 spectrometer. Elemental analyses were performed by the Australian Microanalytical Service, Melbourne.

Acenaphthene was purchased from Fluka, A.G., and recrystallized from ethanol before use. Acenaphthylene was obtained from the same source, and purified by recrystallization from pentane. Diethyl ether, benzene, petroleum ether (bp 58–64°), ethyl acetate, and acetone were purified by standard procedures.

1-Acetoxy-,[41] 1-bromo-,[42–44] 1-chloro-,[45] 1-acetonyl-,[45] 1-phenyl-,[46] 1-methyl-,[46,47] and 1-methoxy acenaphthene,[48] as well as 1-acenaphthenol,[41] diethyl 1-acenaphthenylmalonate,[43] 1-acenaphthenecarbonitrile,[43,49] 1-acenaphthenecarboxylic acid,[43] 1-acenaphthenemalonic acid,[44,45] 1-acenaphtheneacetic acid,[45] ethyl 1-acenaphthenylacetoacetate,[45] trimethyl 1-acenaphthenylammonium bromide,[50] 1-acenaphthenamine,[51] *N*-(1-acenaphthenyl)acetamide,[51] hexachlorobicyclo[2.2.1]heptene,[52] 1,1-dichlorocyclopropane,[53,54] and dibenzobicyclo[2.2.2]octadiene[55,56] were prepared as previously described.

1-Acenaphthenecarboxamide.—1-Acenaphthenecarbonitrile (4.0 g) was warmed at 40–50° with 10 *M* hydrochloric acid (25 ml) for 75 min. Water (300 ml) was added to the solution and the precipitate which formed was separated by filtration and washed with ether and saturated aqueous $NaHCO_3$ solution. The crude product was recrystallized from ethyl acetate and sublimed [130–140° (0.5 mm)] to give colorless crystals of 1-ace-

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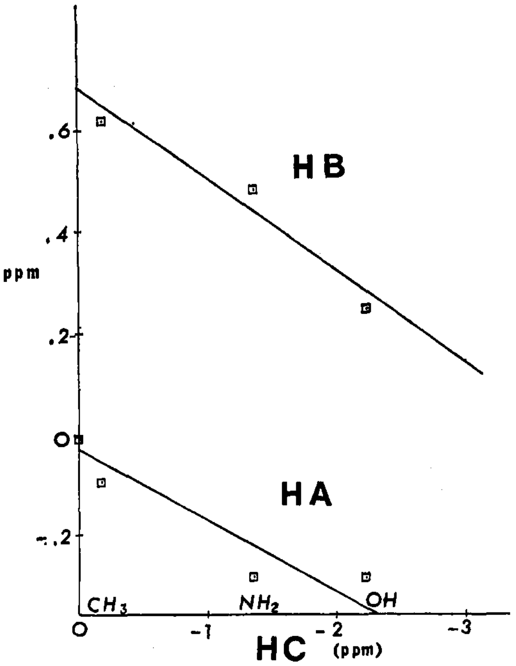

Figure 9.—Plot of H_A *vs.* H_C and H_B *vs.* H_C for substituted acenaphthenes. Similar plots are obtained for cyclopropyl derivatives.

naphthenecarboxamide (2.2 g, 50%): mp 217–218° (sealed tube); uv max (95% C_2H_5OH) 228 nm (ϵ 62,000), 288 (5800), 320 (800); ir ($CHCl_3$) 3520, 3409, 3005, 1680, 1580, 1368, 1052, 1028, 1010, 710 cm^{-1}; nmr ($CDCl_3$) (for signals assigned to benzylic protons, see Table I) δ 4.26 (s, 2, $CONH_2$), 7.08–7.75 (m, 6, aromatics).

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.2; H, 5.65; N, 6.96.

1-*tert*-Butyl-1-acenaphthenol.—A solution of *tert*-butyllithium in ether was prepared from *tert*-butyl chloride (13.7 g), lithium shavings, and dry ether (500 ml).[57] With the temperature at −40°, acenaphthenone (6.0 g) dissolved in a minimum of dry ether was added slowly over 2 hr. The reaction mixture was stirred for a further 2 hr at the same temperature. The lithium addition compound and excess lithium were decomposed by the addition of water. The mixture was extracted with ether (2 × 75 ml) and the combined ether extracts were dried ($MgSO_4$) and concentrated. The crude product was chromatographed on neutral alumina. Benzene eluted acenaphthenone (1.0 g); ether eluted 1-acenaphthenol (1.85 g), and benzene–ether (15%) eluted the crude product (2.1 g), which was rechromatographed to give as a clear oil, 1-*tert*-butyl-1-acenaphthenol (1.6 g, 20%): $n^{25}D$ 1.688; uv max (95% C_2H_5OH) 227 nm (ϵ 73,000), 287 (6800); ir (liquid film) 3450, 3042, 2947, 1592, 1452, 1365, 1012, 817, 797, 778 cm^{-1}; nmr ($CDCl_3$) δ 0.98 [s, 9, $C(CH_3)_3$], 2.15 (s, 1, OH), 3.09 (d, 1, J = 18 Hz, CH_2), 3.79 (d, 1, J = 18 Hz, CH_2), 6.88–7.62 (m, 6, aromatics). *Anal.* Calcd for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 84.8; H, 8.0.

1-*tert*-Butylacenaphthylene.—1-*tert*-Butyl-1-acenaphthenol (0.12 g) was warmed on a steam bath for 2.5 hr with pyridine (1 ml) and thionyl chloride (0.15 g). The reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with 3 *N* sulfuric acid (2 × 20 ml), dilute sodium bicarbonate solution (20 ml), and water. The ethereal extract was dried ($MgSO_4$), concentrated, and filtered through silica gel in light petroleum to give, on evaporation of the solvent, yellow crystals of 1-*tert*-butylacenaphthylene (0.084 g, 84%): mp 38–40°; ir (liquid film) 2900, 1452, 1381, 1263, 1095, 1030, 839, 810, 771, 729, 718 cm^{-1}; nmr ($CDCl_3$) δ 1.48 [s, 9, $C(CH_3)_3$], 6.71 (s, 1, C=CH), 7.13–7.87 (m, 6, aromatics). *Anal.* Calcd for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 92.2; H, 7.9.

1-*tert*-Butylacenaphthene.—A solution of 1-*tert*-butylacenaphthylene (0.10 g) in absolute ethanol was hydrogenated over Raney nickel at room temperature under 2 atm of hydrogen. The reaction mixture was filtered and the solvent was removed

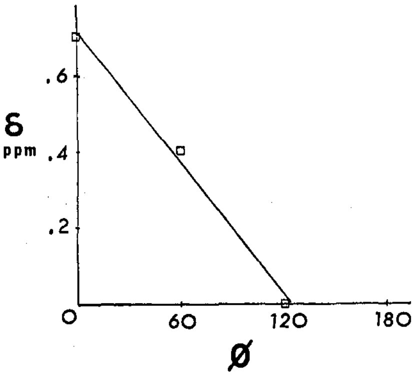

Figure 10.—Plot of backbonding contribution to β chemical shifts as a function of dihedral angle (ϕ).

to give colorless crystals of 1-*tert*-butylacenaphthene (0.095 g, 95%). The compound was further purified by filtration through silica gel in light petroleum: mp 37–38°; uv max (95% C_2H_5OH) 227 nm (ϵ 76,000), 287 (6800); ir (liquid film) 3040, 2944, 2857, 1580, 1484, 1450, 1395, 1369, 1210, 832, 806, 779 cm^{-1}; nmr ($CDCl_3$) δ 0.92 [s, 9, $C(CH_3)_3$] (see Table I for benzylic protons), 6.95–7.62 (m, 6, aromatics). *Anal.* Calcd for $C_{16}H_{18}$: C, 91.4; H, 8.6. Found: C, 91.2; H, 8.9.

Methyl 1-Acenaphthenecarboxylate.—A saturated solution of diazomethane in ether (0°) was added to a mixture of 1-acenaphthenecarboxylic acid (0.5 g) in methanol (20 ml) at 0°. The reaction mixture was allowed to stand at room temperature for 30 min before the solvent was evaporated. The residue was chromatographed on silica gel in light petroleum to give a thick oil which became crystalline on standing in the refrigerator for several days. This was rechromatographed to yield colorless crystals of methyl 1-acenaphthenecarboxylate (0.4 g, 75%): mp 31–33°; uv max (95% C_2H_5OH) 227 nm (ϵ 71,000), 288 (6800); ir ($CHCl_3$) 3040, 3008, 2956, 1731, 1601, 1432, 1320, 1267, 1165, 1030, 840 cm^{-1}; nmr ($CDCl_3$) δ 3.72 (s, 3, $COOCH_3$) (for signals assigned to benzylic protons see Table I), 7.15–7.70 (m, 6, aromatics). *Anal.* Calcd for $C_{14}H_{12}O_2$: C, 79.2; H, 5.6. Found: C, 79.3; H, 5.5.

1-Methylacenaphthene-*3,5,6,8*-d_4.—1-Methylacenaphthene (0.5 g) was heated at reflux in deuteriotrifluoroacetic acid (7.5 ml), carbon tetrachloride (2.5 ml), and difluorophosphonic acid (0.05 ml) for 3 days. The solvent was evaporated and the crude product was chromatographed on neutral alumina to yield 1-methylacenaphthene-*3,5,6,8*-d_4 (0.10 g, 65%), nmr ($CDCl_3$) δ 1.33 (d, 3, CH_3) (for signals assigned to benzylic protons see Table I), 7.32 (s, 2, $H_{4,7}$).

Additional Notes.—Two papers[58,59] have appeared since this manuscript was completed which should be considered in conjunction with this work. Wiberg, *et al.*,[58] have reported detailed data for cyclopropyl derivatives which can be added to Table VI. They also note the substrate dependence of α-proton chemical shifts, and the general correlation of coupling constants with electronegativity. Their assignment of the β-proton shifts to anisotropy effects appears questionable. The discussion by Boaz[59] of chemical shifts in terms of electric dipole contributions appears to us to have more merit.

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Registry No.—1-*tert*-butyl-1-acenaphthenol, 40748-33-2; 1-*tert*-butylacenaphthylene, 38206-03-0.

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Supplementary Material Available.—A table of analysis results for 1-methylacenaphthene and three figures will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-3122.

A Novel Reaction between 3,5-Dinitroacetophenone–Acetone and Secondary Amines Yielding Naphthalenic Structures

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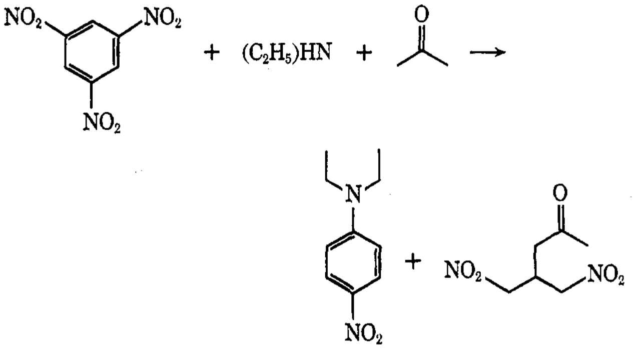
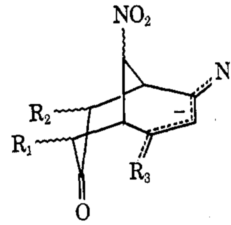
The exothermic reaction which occurs upon the addition of a secondary amine to a mixture of 3,5-dinitroacetophenone and acetone was investigated to determine the nature of the products. Instead of the expected Meisenheimer addition product, a new compound, 1-methyl-3-diethylamino-5,7-dinitronaphthalene, was formed. Employing 3,5-dinitrobenzaldehyde as the starting material resulted in the formation of the analogous 1,3-dinitro-7-diethylaminonaphthalene. The scope of the reaction is investigated.

The chemistry of complexes arising from the interaction of electron-deficient aromatics with organic bases has received considerable attention during the last 10 years and has been reviewed.[1,2] These so-called Meisenheimer complexes in which the negative charge is delocalized over a pentadienide system have been observed under certain conditions to undergo an internal cyclization to form a second bond and a stable bicyclic anion. An example is the reaction between trinitrobenzene, acetone, and diethylamine.



Although, as shown above, the products usually isolated are *N*,*N*-diethyl-*p*-nitroaniline and 2-acetonyl-1,3-dinitropropane,[3] the intermediate complex Ia can be isolated under special conditions.[4] Such structures with electron-withdrawing substituents other than nitro and ketones other than acetone have been isolated (Ib, Ic).[5]



Ia, $R_1 = R_2 = H$; $R_3 = NO_2$
b, $R_1 = COCH_3$; $R_2 = H$; $R_3 = NO_2$
c, $R_1 = CO_2Et$; $R_2 = H$; $R_3 = CN$

Analogous products and intermediates might be expected from the reaction of 3,5-dinitroacetophenone, acetone, and alkylamines. It was hoped to obtain some otherwise difficultly available acetophenones by means of this reaction.

In fact, when diethylamine is added to an acetone solution of 3,5-dinitroacetophenone, the mixture immediately turns black and a mildly exothermic reaction takes place. After a few minutes at room temperature black crystals begin to appear, their formation being complete within 1 hr, yielding a compound (mp 178–180° from dioxane–water) hereafter referred to as compound Y (Table I).

TABLE I

COMPOUND Y

Nmr (CF_3CO_2D)				Uv (MeOH)		Uv (66% H_2SO_4)	
δ	H	Multiplicity	*J*	λ	ε	λ	ε
0.8	6	Triplet	7.0 Hz				
3.4	4	Quartet	7.0 Hz	235	27,000	210	40,000
2.5	3	Singlet		260	48,000	255	21,000
7.4[a]	1	Broad singlet		350	5,800	295	14,000
8.4[a]	1	Broad singlet		415	24,000	360	2,700
8.6[a]	1	Doublet	2.0 Hz	470	25,000	430	80
8.9[a]	1	Doublet	2.0 Hz	620	~0	550	~0

[a] The chemical shifts of these four protons are extremely solvent dependent, being well separated in trichloroacetic acid and mineral acids but having totally different positions in other solvents. For example, in chloroform or methylene chloride the two downfield protons accidentally overlap (2 H, δ 8.36), the two upfield protons now appearing at δ 7.5 and 7.1; while in dimethyl sulfoxide both the two downfield protons as well as the two upfield protons are accidentally overlapping at δ 8.7 and 7.3, respectively.

Elemental analysis established the empirical formula as $C_{15}H_{17}N_3O_4$ and a mass spectrum of the compound confirms it to have a molecular weight of 303. This corresponds to the combination of 1 equiv each of diethylamine, acetone, and 3,5-dinitroacetophenone, together with the loss of 1 molar equiv of hydrogen and water. The ir of Y shows the presence of acidic hydrogens or C=N multiple bonds. The uv of Y shows it not to be of the dinitropropenyl class, as such

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