The Proton Resonance Spectra of Heterocycles. Part VIII.[1] Substituent Effects on Coupling Constants in Bicyclic Heteroaromatic Compounds and the Prediction of Chemical Shifts from Coupling Constants

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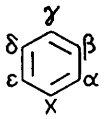
Substituents affect coupling constants in bicyclic heteroaromatic compounds: they increase $^3J_{\alpha\beta}$ and $^4J_{\alpha\epsilon}$, slightly decrease $^4J_{\alpha\gamma}$ and $^5J_{\alpha\delta}$ and have little effect on $^3J_{\beta\gamma}$. The regularities disclosed allow prediction of J in substituted systems. *ortho*-Substituent effects on chemical shifts relate to the corresponding ^3J values in the unsubstituted compound, reflecting the dependence of both on partial bond fixation.

SUBSTITUENT effects on coupling constants for polysubstituted benzenes are additive,[2-5] and the pattern quite well recognised;[6] coupling constants for unsubstituted polycyclic aromatic compounds vary with bond fixation in a logical manner.[7,8] However, substituent effects on coupling constants in polycyclic heteroaromatic compounds have been little investigated (for polycarbocyclic compounds see ref. 9). Recently,[1] we found that, for certain 5- and 6-monosubstituted-benzoxazoles, -benzothiazoles, and -benzoselenazoles, the effect of the substituent on the coupling constants could be predicted from the corresponding monosubstituted benzene by equation (1), where J_X is the coupling constant in the substituted, and J_H in the corresponding unsubstituted compound. We now extend this work.

$$J_X^{\mathrm{arom}} - J_H^{\mathrm{arom}} = J_X^{\mathrm{benz}} - J_H^{\mathrm{benz}} \qquad (1)$$



(1)

The quantities $J_X - J_H$ are defined as ' substituent coupling constants ' (SCC) and the SCC in question is indicated by two of the Greek letters of structure (1). Results are reported in Table 1 for a variety of substituents and systems. A clear pattern is disclosed, as is summarised in Table 2. The effects of all types of substituents are qualitatively similar; significant increases in $J_{\alpha\beta}$ and $J_{\alpha\epsilon}$, with smaller decreases in $J_{\alpha\gamma}$ and $J_{\alpha\delta}$ and little change in $J_{\beta\gamma}$. The atom adjacent to the ring appears to dominate the magnitude of the effect: O,N > Cl > C. Such behaviour has been previously recognised[10] for monocyclic compounds.

$$\mathrm{SCS}^{\mathrm{arom}} = a\mathrm{SCS}^{\mathrm{benz}} + b \qquad (2)$$

Relation between Substituent Chemical Shifts (SCS) and Coupling Constants.

—We have shown previously,[1,11] that equation (2) relates the SCS for a heterocyclic system to the corresponding SCS for benzene. For *ortho*-SCS, the values of a depend on bond order, and hence on the degree of bond fixation for bicyclic heteroaromatic systems. In particular, for the SCS at a ' conjugated ' *ortho*-position (in an $\cdot\mathrm{CX}{:}\mathrm{CH}\cdot$ relationship), the constant a which we here denote a_c, is >1, whereas at a ' nonconjugated ' *ortho*-position (in an ${:}\mathrm{CX}\cdot\mathrm{CH}{:}$ relationship) $a_s < 1$. The *ortho*-SCS thus varies with bond order.

$$(\Delta\tau)_{a\mathrm{X}b} = n_{\mathrm{X}}J_{ab} + t_{\mathrm{X}} \qquad (3)$$

Now, *ortho*-coupling constants also vary with bond order. The ratio $^3J^{\mathrm{arom}}/^3J^{\mathrm{benz}}$ is a measure of the partial bond fixation,[7] varying from zero where $^3J^{\mathrm{arom}}/^3J^{\mathrm{benz}} = 1$ as in benzene, to complete where $^3J^{\mathrm{arom}}/^3J^{\mathrm{benz}} = 0{\cdot}64$ as in cyclohexadiene. For a bicyclic aromatic system, a relation was therefore sought between the SCS and the coupling constants for the parent ring system (Table 3). We originally proposed[12] equation (3) but we now argue that the quantity $(a_c - a_s)/a_c$ (which measures the deviation of a_s/a_c from unity, *i.e.* perfect bond delocalisation) should be proportional to $(^3J_c - {}^3J_s)/^3J$ (which measures the deviation of $^3J_s/^3J_c$ from unity), where ^3J_c and ^3J_s are the *ortho*-coupling constants across the ' conjugated ' and ' non-conjugated ' positions in the unsubstituted parent compound. Such a relation is expressed in equation (4). Data are recorded in

$$(a_c - a_s)/a_c = m(^3J_c - {}^3J_s)/^3J_c \qquad (4)$$

Table 4 and plotted in Figure 1: the slope is $m = 1{\cdot}5$

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[1] Part VII, see A. R. Katritzky and Y. Takeuchi, *Org. Mag. Res.*, 1970, **2**, 569.

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[10] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

[11] A. R. Katritzky, Y. Takeuchi, B. Ternai, and G. J. T. Tiddy, *Org. Mag. Res.*, 1970, **2**, 357.

[12] A. R. Katritzky, B. Ternai, and G. J. T. Tiddy, *Tetrahedron Letters*, 1966, 1713.

(correlation coefficient 0·84), and the intercept 0·14. Extrapolation of the line to $(^3J_c - {}^3J_s)/{}^3J_c = 0{\cdot}36$, *i.e.* complete bond fixation, gives $(a_c - a_s)/a_c = 0{\cdot}68$, *i.e.* $a_c = 1{\cdot}68a_s$.

In addition to the relation (4), the values of both a_c and a_s are linearly related to the corresponding ^3J_c or ^3J_s by relation (5), which is shown graphically in Figure 2 (correlation coefficient 0·963).

$$a = 0{\cdot}357 \times {}^3J - 1{\cdot}64 \qquad (5)$$

Conclusions.—Using the correlations established in this paper, it should be possible to predict chemical shifts and coupling constants in substituted heterocyclic compounds from the parameters of the parent molecule, or *vice versa*. This should be of considerable utility *inter alia* in the elucidation of complex patterns by enabling reasonable 'guessed' parameters to be used in an iterative procedure. For example, if the *ortho*-coupling constants are known, or can be estimated, for a parent heterocyclic ring system, then use of equation (5) and the SCS for benzene gives estimated *ortho*-SCS for a substituted compound that can be used as computer input.

TABLE 1

Substituent coupling constant (SCC) values for various aromatic systems (Hz)

Subst.	Ring system	Subst. position	*ortho*		*meta*		*para*	Solvent	Ref.
			αβ	βγ	αγ	αε	αδ		
NH_2	Benzene		0·46	−0·13	−0·26	1·08	−0·19	Neat	*a*
	Naphthalene	2	0·4			1·3	?	C_6H_{12}	*b*
	Quinoline	8	0·93	0·0	−0·25			Me_2SO	*c*
	Quinoline	8	1·08	+0·13	−0·39			Me_2CO	*c*
	Quinoxaline	5	0·8	−0·2	−0·2			Me_2SO	*d*
	Quinoxaline	6	0·6			1·3	−0·5	Me_2SO	*d*
NMe_2	Benzene		0·86	−0·25	−0·37	1·33	−0·20	Neat	*a*
	Benzo-2,1,3-selenadiazole	5	0·73			1·45	−0·61	$CDCl_3$	*e*
OH	Benzene		0·61	−0·14	−0·29	1·33	−0·19	CCl_4	*f*
	Naphthalene	2	0·5			0·8	?	Me_2SO	*c*
	Naphthalene	2	0·5			1·0	?	Me_2CO	*c*
	Quinoline	5	0·73	0·2	−1·0(?)			Me_2SO	*c*
	Quinoline	8	0·78	−0·05	−0·35			Me_2SO	*c*
	Quinoline	8	1·38	0·33	−0·79(?)			Me_2CO	*c*
	Quinoline	8	0·78	0·15	−0·20			$CDCl_3$	*c*
	Quinazoline	5	1·29	−0·10	−0·63			Me_2SO	*g*
	Quinazoline	6	0·80			1·25	−0·50	Me_2SO	*g*
	Quinazoline	7	0·49			0·77	0·20	Me_2SO	*g*
	Quinazoline	8	0·69	−0·01	0·15			Me_2SO	*g*
	Quinoxaline	5	0·70	−0·20	−0·10			Me_2SO	*d*
	Quinoxaline	5	0·58	0·04	−0·18			Me_2CO	*c*
OMe	Benzene		0·77	−0·10	−0·31	1·35	−0·31	Neat	*a*
	Naphthalene	2	0·5			1·3	?	C_6H_{12}	*b*
	Quinazoline	5	1·29	−0·30	−0·63			Me_2SO	*g*
	Quinazoline	6	1·0			1·55	−0·50	Me_2SO	*g*
	Quinazoline	7	0·79			1·17	0·30	Me_2SO	*g*
	Quinazoline	8	0·79	0·09	−0·05			Me_2SO	*g*
	Quinoxaline	6	0·7			1·3	−0·10	Me_2SO	*d*
	Benzofuroxan	5	−0·10(?)			1·05	−0·10	Me_2CO	*h*
	Benzofuroxan	6	0·6			1·25	−0·70	Me_2CO	*h*
	Benzo-2,1,3-selenadiazole	5	1·38			1·00	−0·90	$CDCl_3$	*e*
	Quinoxaline *	5	1·2	0·0	−0·7			Me_2SO	*d*
	Quinoxaline *	5	0·98	0·20	−0·18			Me_2CO	*c*
OAc	Benzene		0·63	−0·11	−0·25	1·13	−0·19	Neat	*a*
	Quinoxaline	5	0·6	−0·1	−0·2			Me_2SO	*d*
	Quinoxaline	5	0·70	0·26	−0·17			Me_2CO	*c*
	Quinoxaline	6	0·5			1·2	−0·4	Me_2SO	*d*
	Quinoxaline	6	0·65			1·21	−0·16	Me_2CO	*c*
Me	Benzene		0·12	−0·08	−0·11	0·59	−0·06	Neat	*i*
	Naphthalene	2	?			0·7	?	C_6H_{12}	*b*
	Quinoline	6	0·10			0·65	−0·15	Me_2SO	*c*
	Quinoline	6	0·09			0·36	0·02	Me_2CO	*c*
	Quinoline	6	0·05			0·75	−0·10	$CDCl_3$	*c*
	Quinoline	8	−0·02	−0·20	0·10			Me_2SO	*c*
	Quinoline	8	0·23	−0·15	0·00			Me_2CO	*c*
	Quinazoline	7	0·19			0·07	0·10	Me_2SO	*g*
	Quinazoline	8	0·49	−0·11	−0·15			Me_2SO	*g*
	Quinoxaline	5	−0·10	−0·50	0·10			Me_2SO	*d*
	Quinoxaline	5	0·14	0·42	−0·53			Me_2CO	*c*
	Quinoxaline	6	0·20			0·9	−0·5	Me_2SO	*d*
	Benzofuroxan	4	0·20	0·15	−0·05			$CDCl_3$	*j*
	Benzofuroxan	5	−0·10			0·48	−0·20	$CDCl_3$	*j*
	Benzofuroxan	6	−0·10			0·45	−0·20	$CDCl_3$	*j*
	Benzofuroxan	7	0·20	−0·3	0·0			$CDCl_3$	*j*
	Benzo-2,1,3-selenadiazole	5	0·31			0·33	0·08	$CDCl_3$	*e*

TABLE 1 (*Continued*)

Subst.	Ring system	Subst. position	*ortho* $\alpha\beta$	*ortho* $\beta\gamma$	*meta* $\alpha\gamma$	*meta* $\alpha\varepsilon$	*para* $\alpha\delta$	Solvent	Ref.
Cl	Benzene		0·49	0·12	−0·21	0·89	−0·24	Neat	*a*
	Quinazoline	6		0·0		0·75	−0·50	Me_2SO	*g*
	Quinazoline	7	0·49			0·57	−0·20	Me_2SO	*g*
	Quinazoline	8	0·99	−0·01	−0·15			Me_2SO	*g*
	Quinoxaline	6	0·50			1·0	−0·20	Me_2SO	*d*
	Benzofuroxan	5	0·30			0·85	−0·3	Me_2CO	*h*
	Benzofuroxan	6	−0·10			0·45	−0·40	Me_2CO	*h*
	Benzo-2,1,3-selenadiazole	5	0·35			0·85	−0·10	$CDCl_3$	*e*
CO_2Me	Benzene		0·32	−0·04	−0·07	0·47	−0·07	Neat	*a*
	Quinoline	6	0·3			0·65	−0·05	Me_2SO	*c*
	Quinoline	6	0·29			0·61	0·12	Me_2CO	*c*
	Quinoxaline †	6	0·2			0·5	−0·3	Me_2SO	*d*
	Quinoxaline †	6	0·43			0·51	−0·01	Me_2CO	*c*
	Benzofuroxan †	5	0·5			0·45	−0·1	Me_2CO	*h*
	Benzofuroxan †	6	0·3			0·25	−0·1	Me_2CO	*h*
NO_2	Benzene		0·79	−0·10	−0·21	1·08	−0·20	Neat	*a*
	Quinoline	5	0·83	0·0	−0·4			Me_2SO	*c*
	Quinoline	6	0·7			1·05	−0·15	Me_2SO	*c*
	Quinazoline	5	1·09	0·40	−0·63			Me_2SO	*g*
	Quinazoline	6	1·30			1·25	0·10	Me_2SO	*g*
	Quinazoline	8	0·99	0·19	−0·15			Me_2SO	*g*
	Quinoxaline	6	0·7	−0·4		1·2		Me_2SO	*d*

* Data for OEt. † Data for CO_2Et

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TABLE 2

Substituent coupling constants (mean and standard deviation) (Hz)

Substituent	*ortho* $\alpha\beta$	*ortho* $\beta\gamma$	*meta* $\alpha\gamma$	*meta* $\alpha\varepsilon$	*para* $\alpha\delta$
NH_2	0·71 ± 0·25	−0·05 ± 0·13	−0·28 ± 0·07	1·23 ± 0·10	−0·35 ± 0·16
NMe_2	0·80 ± 0·07	−0·25	−0·37	1·39 ± 0·06	−0·41 ± 0·21
OH	0·76 ± 0·27	0·02 ± 0·16	−0·23 ± 0·22	1·03 ± 0·23	−0·16 ± 0·29
OMe	0·91 ± 0·27	−0·02 ± 0·17	−0·37 ± 0·25	1·25 ± 0·16	−0·33 ± 0·38
OAc	0·62 ± 0·07	0·02 ± 0·17	−0·21 ± 0·03	1·18 ± 0·04	−0·25 ± 0·11
Me	0·13 ± 0·15	−0·10 ± 0·26	−0·08 ± 0·19	0·53 ± 0·23	−0·11 ± 0·17
Cl	0·43 ± 0·30	0·04 ± 0·06	−0·18 ± 0·03	0·77 ± 0·18	−0·28 ± 0·13
CO_2Me	0·33 ± 0·09	−0·04	−0·07	0·49 ± 0·12	−0·07 ± 0·12
NO_2	0·91 ± 0·21	0·02 ± 0·27	−0·35 ± 0·19	1·15 ± 0·08	−0·08 ± 0·13

TABLE 3

Coupling constants of unsubstituted heteroaromatic compounds

Ring system	J_{45}	J_{46}	J_{47}	J_{56}	J_{57}	J_{58}	J_{67}	J_{68}	J_{78}	Solvent	Ref.
Naphthalene				8·2		6·9	6·9		8·2	CCl_4	*a*
Naphthalene				8·6	1·4			1·4	8·6	C_6H_{12}	*b*
Quinoline				8·30	1·45	0·65	6·97	1·6	8·4	Me_2SO	*c*
Quinoline				8·07	1·49	0·48	6·82	1·10	8·41	Me_2CO	*d*
Quinoline				8·15	1·45	0·70	6·92	1·20	8·55	$CDCl_3$	
Quinazoline				8·21	1·45	0·70	6·71	1·43	8·40	Me_2SO	
Quinoxaline				8·6	1·4	0·8	7·1	1·4	8·6	Me_2SO	
Quinoxaline				8·40	1·46	0·60	6·94	1·46	8·40	Me_2CO	
Benzofuroxan	9·3	0·75	1·1	6·4	0·95		9·1			Me_2CO	
Benzo-2,1,3-selenadiazole	9·09	1·20	0·94	6·51	1·20		0·09			$CDCl_3$	

[a] B. Dischler and G. Englert, *Z. Naturforsch.*, 1961, **16***A*, 1180. [b] Y. Sasaki and M. Suzuki, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 1090. [c] This study. [d] P. J. Black and M. L. Heffernan, *Austral. J. Chem.*, 1964, **17**, 558.. [e] P. J. Brignell, A. R. Katritzky, R. E. Reavill, G. W. H. Cheeseman, and A. A. Sarsfield, *J. Chem. Soc.* (*B*), 1967, 1241. [f] P. J. Black and M. L. Heffernan, *Austral J. Chem.*, 1965, **18**, 707. [g] R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.*, 1963, 197. [h] N. M. D. Brown and P. Bladon, *Spectrochim. Acta*, 1968, **24***A*, 1869.

TABLE 4

Substituent effects on coupling constants and chemical shifts for various benzo-fused heteroaromatic systems

Ring system	Subst. position	a_c	a_s	$(a_c - a_s)/a_c$	Solvent	Ref.	^3J_c	^3J_s	$(^3J_c - {}^3J_s)/{}^3J_c$	Solvent	Ref.	m
2-Methylbenzothiazole	5	1·10	0·86	0·218	Me_2SO	*a*	8·1	7·2	0·111	Me_2SO	*a*	1·96
Benzo[*b*]thiophen	5	1·08	0·80	0·259	Me_2CO	*b*	7·75	7·25	0·065	CCl_4	*k*	4·02
Naphthalene	2	1·36	0·76	0·441	CCl_4	*c*	8·2	6·9	0·159	CCl_4	*l*	2·78
Quinoline	6	1·37	0·84	0·387	CCl_4, C_6H_{12}	*d*	8·55	6·92	0·191	C_6H_{12}	*a*	2·03
Quinazoline	7	1·46	0·92	0·370	Me_2SO	*e*	8·4	6·7	0·202	Me_2SO	*a*	1·83
Quinoxaline	6	1·51	0·79	0·477	Me_2SO	*f*	8·6	7·1	0·174	Me_2SO	*f*	2·73
Quinoxaline	6	1·29	0·70	0·457	CCl_4, C_6H_{12}	*d*	8·4	6·9	0·179	CCl_4	*m*	2·56
1-*p*-Nitrophenyl-3-methylindazole	5	1·25	0·71	0·432	Me_2CO	*g*	8·0	6·5	0·188	Me_2CO	*n*	2·30
1-*p*-Nitrophenyl-3-methylindazole	6	1·20	0·79	0·342	Me_2CO	*g*	8·0	6·5	0·188	Me_2CO	*n*	1·82
Benzofurazan-1-oxide [o]	5	1·58	0·78	0·506	Me_2CO, $CDCl_3$	*h*, *i*	9·3	6·4	0·312	Me_2CO	*h*	1·62
Benzofurazan-1-oxide [o]	6	1·65	0·65	0·606	Me_2CO, $CDCl_3$	*h*, *i*	9·1	6·4	0·297	Me_2CO	*h*	2·04
Benzo-2,1,3-selenadiazole	5	1·69	0·55	0·675	$CDCl_3$	*j*	9·1	6·5	0·286	$CDCl_3$	*j*	2·36

[a] This study. [b] B. Caddy, M. Martin-Smith, R. K. Norris, S. T. Reid, and S. Sternhell, *Austral. J. Chem.*, 1968, **21**, 1853. [c] Y. Sasaki and M. Suzuki, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 1090. [d] Y. Sasaki and M. Suzuki, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 1799. [e] A. R. Katritzky, R. E. Reavill, and F. J. Swinbourne, *J. Chem. Soc.* (*B*), 1966, 351. [f] P. J. Brignell, A. R. Katritzky, R. E. Reavill, G. W. H. Cheeseman, and A. A. Sarsfield, *J. Chem. Soc.* (*B*), 1967, 1241. [g] E. B. Dennler, C. R. Portal, and A. R. Frasca, *Spectrochim. Acta*, 1967, **23***A*, 2243. [h] R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.*, 1963, 197. [i] A. J. Boulton, A. R. Katritzky, M. J. Sewell, and B. Wallis, *J. Chem. Soc.* (*B*), 1967, 914; A. J. Boulton, P. J. Halls, and A. R. Katritzky, *ibid.*, 1970, 636. [j] N. M. D. Brown and P. Bladon, *Spectrochim. Acta*, 1968, **24***A*, 1869. [k] K. Takahashi, I. Ito, and Y. Matsuki, *Bull. Chem. Soc. Japan*, 1966, **39**, 2316. [l] B. Dischler and G. Englert, *Z. Naturforsch.*, 1961, **16***A*, 1180. [m] P. J. Black and M. L. Heffernan, *Austral. J. Chem.*, 1965, **18**, 707. [n] Data for 1-methylindazole. See J. Elguero, A. Fruchier, and R. Jacquier, *Bull. Soc. chim. France*, 1966, 2075. [o] No time-averaging.

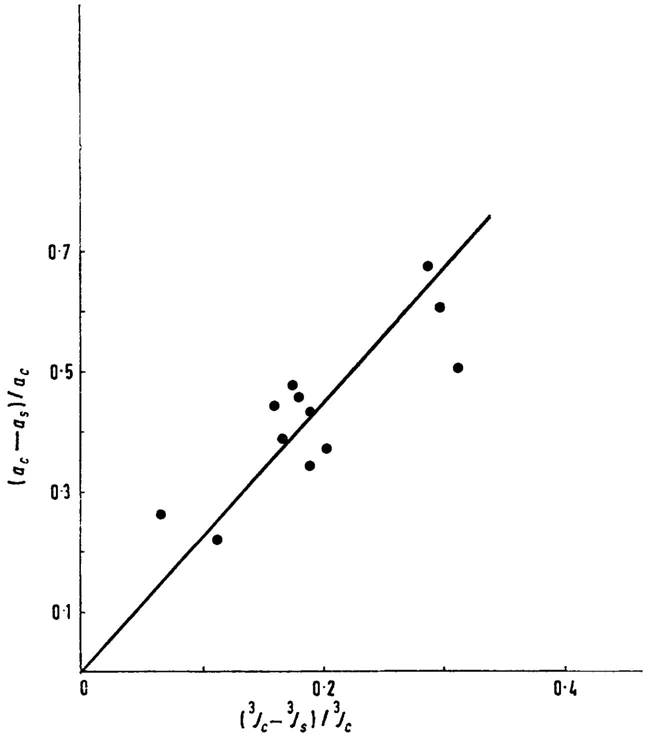

FIGURE 1 Plot of $(a_c - a_s)/a_c$ *vs.* $(^3J_c - {}^3J_s)/{}^3J_c$

EXPERIMENTAL

Spectra were measured on an HA-100 Varian Spectrometer with sample spinning as *ca.* 10% w/v solutions (for details see Table 1). Compounds were commercial specimens or prepared by standard methods: they were characterised by m.p. or gas chromatography and by their n.m.r. spectra. Spectral analyses were carried out by iterative computation using the program LAOCN3.[13]

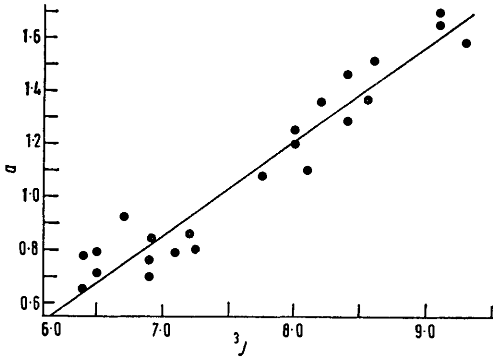

FIGURE 2 Plot of *a* against ^3J; the line drawn is that of equation (5)

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[13] A. A. Bothner-By and S. M. Castellano, 'Computer Programs for Chemistry,' ed. D. F. De Tar, Benjamin, New York, 1968, vol. 1, p. 16.