requirements of the alkyl or phenyl group.[6a,b,10] The coordination of the europium in these systems occurs at the phosphoryl oxygen.[3,11] Apparently, the nature of the phosphoryl bond is modified thereby, and the balance of steric and electronic interactions is changed such that equatorial phosphoryl preference is reduced. Obviously, 1,3-syn-axial steric interactions do not of themselves control conformation, since coordination should somewhat increase the steric size of the phosphoryl oxygen. Also, a tighter Eu–phosphorus complex might be expected with the P═O of **2a** or **3a** than with that of conformer **2b** or **3b**, again for steric reasons. Thus, various attractive and repulsive vicinal interactions about the P–O single bonds in the ring appear to be of considerable importance in controlling conformation here as well as in the corresponding cyclic trivalent systems.[12]

Acknowledgment. Support of this work by the National Science Foundation (GP 22885) is gratefully acknowledged.

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(11) T. M. Ward, I. L. Allcox, and G. H. Wahl, Jr., *Tetrahedron Lett.*, 4421 (1971); E. D. Cuddy, K. Treon, and B. J. Walker, *ibid.*, 4433 (1971); J. K. M. Saunders and D. H. Williams, *ibid.*, 2813 (1971); J. R. Corfield and S. Trippett, *Chem. Commun.*, 721 (1971); Y. Kashman and O. Awerbouch, *Tetrahedron*, 27, 5593 (1971).

(12) C. L. Bodkin and P. Simpson, *Chem. Commun.*, 829 (1969); D. W. White, G. K. McEwen, and J. G. Verkade, *Tetrahedron Lett.*, 5369 (1968); D. W. White, R. D. Bertrand, G. K. McEwen, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 7125 (1970); J. H. Hargis and W. G. Bentrude, *ibid.*, **92**, 7136 (1970); W. G. Bentrude and K. C. Yee, *Tetrahedron Lett.*, 3999 (1970); W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, **93**, 797 (1971); C. L. Bodkin and P. Simpson, *J. Chem. Soc. B*, 1136 (1971).

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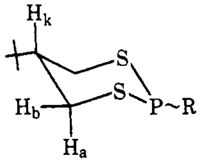
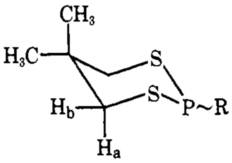
Conformational Analysis of 2-Phospha-1,3-dithiacyclohexanes. Further Evidence for the General Axial Preference of Phosphorus Substituents in Saturated Six-Membered Rings

Sir:

In cyclohexyl systems and in saturated six-membered heterocycles most substituents prefer to adopt equatorial conformations, primarily because of severe 1,3 cross-ring steric interactions encountered when the groups are axial.[1] On the contrary, there is increasing evidence that in 2-phospha-1,3-dioxacyclohexanes[2,3] and in phosphacyclohexanes[4] substituents on phosphorus, including alkyl[3c] and aryl[2,4a] groups, strongly prefer and are unconstrained in axial conformations. This communication reports our preliminary findings on the conformational analysis of 2-R-2-phospha-1,3-dithiacyclohexanes (I and II), which furnish further testimony for the intriguing axial preference of phosphorus substituents in six-membered rings.



I



II

a, R = Ph
b, R = OMe
c, R = Me
d, R = Et
e, R = *t*-Bu

The 2-phenyl-5-*tert*-butyl derivative Ia was obtained and was found to be a mixture of cis and trans isomers in an 85/15 (or 15/85) ratio. The isomers in the mixture were differentiated by the *tert*-butyl resonance in the pmr spectrum (δ ($CDCl_3$) major, 0.76; minor, 0.99 ppm). The major isomer (Ia1) was readily separated by fractional crystallization (MeOH), mp 94–95°, $\delta_{^{31}P}$ (C_6H_6) −28.9 ppm, but attempts to purify the minor isomer (Ia2) have thus far been fruitless.

That the major isomer was the thermodynamically more stable one was verified by thermal equilibration monitored by pmr. At 200° equilibrium was attained in *ca.* 7 hr and the final ratio was Ia1/Ia2 = 84.5/15.5. The thermal stereomutation process was found to be accelerated by traces of acid.[5] The following equilibrium data were obtained: $K_{175^\circ} = 6.9$, $K_{200^\circ} = 5.6 \pm 0.2$, and $K_{225^\circ} = 4.8$, which give the respective free energies, $\Delta G = -1.67$, -1.59, and -1.55 kcal/mol (ΔG_{25° = =1.91 ± 0.2 kcal/mol).[6] Kinetics were measured under acid-free conditions at these temperatures and it was established that the activation energy ($\Delta G^{\ddagger}{}_{298}$) for phosphorus inversion in Ia is *ca.* 31 kcal/mol.[7]

Analysis of the proton nmr spectrum of Ia1 in $CDCl_3$ at 220 MHz revealed an approximately first-

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(1) Exceptions to this include systems in which (a) the presence of heteroatoms causes a great reduction of axial–axial repulsions: L. Angiolini, R. P. Duke, R. A. Y. Jones, and A. R. Katritzky, *Chem. Commun.*, 1308 (1971), and references therein; (b) strain is encountered by vicinal equatorial group interactions: E. L. Eliel, L. D. Kopp, J. E. Dennis, and S. A. Evans, Jr., *Tetrahedron Lett.*, 3409 (1971); (c) dipole–dipole interactions force polar groups into an axial position: R. U. Lemieux, *Pure Appl. Chem.*, **25** (3), 527 (1971); N. S. Zefirov and N. M. Shekhtman, *Russ. Chem. Rev.*, 40 (4), 315 (1971); E. L. Eliel, *Spec. Lect., XXIIIrd Int. Congr. Pure Appl. Chem.*, **7**, 219 (1971); E. L. Eliel and M. K. Kaloustian, *Chem. Commun.*, 290 (1970); (d) other strain factors are operative: F. Johnson and D. T. Dix, *J. Amer. Chem. Soc.*, **93**, 5931 (1971).

(2) W. G. Bentrude and K. C. Yee, *Tetrahedron Lett.*, 3999 (1970).

(3) (a) M. Haemers, R. Ottinger, J. Reisse, and D. Zimmerman, *ibid.*, 461 (1971); (b) W. G. Bentrude and J. H. Hargis, *J. Amer. Chem. Soc.*, **92**, 7136 (1970); W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *ibid.*, **93**, 797 (1971); C. L. Bodkin and P. Simpson, *J. Chem. Soc. B*, 1136 (1971). See also references in ref 1.

(4) (a) A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Amer. Chem. Soc.*, **93**, 2575 (1971); A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr., and L. D. Quin, *Chem. Commun.*, 1020 (1971); J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron*, **27**, 4245 (1971).

(5) Equilibrium of pure Ia1 under conditions where acid was punctiliously eliminated was complete in *ca.* 20 hr at 200° and gave the same final isomer ratio.

(6) Although the amount of the minor isomer (Ia2) present was insufficient for pmr analysis, the difference in the *tert*-butyl resonances for Ia1 and Ia2 indicates different environments in the two isomers and suggests that Ia2 is either in a chair conformation with an axial 5-*tert*-butyl or possibly in a twist form. A plot of ln K_{eq} *vs.* $1/T$ and a least-squares fit of the data gave the values, $-\Delta H = 2.4$ kcal/mol; $\Delta S = 1.8$ eu. The relatively small entropy difference points toward a mixture of chair conformations (*i.e.*, entropy of mixing) but we do not regard the limited data to be of sufficient precision to rule out twist forms of higher entropy.

(7) The value for $\Delta G^{\ddagger}$ is in accord with anticipated inversion barrier for this system: A. Rauk, J. D. Androse, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6507 (1971).

Table I. Proton Nmr Data for 2-R-5,5-Dimethyl-2-phospha-1,3-dithiacyclohexanes[a]

Compd	Solvent	δ_{Me}(ax)		δ_{Me}(eq)	δ_{CH_2}(b)[c]		δ_{CH_2}(a)[c]	$^3J_{Pa}$[b]	$^3J_{Pb}$[b]
IIa	$CDCl_3$	1.30	(0.50)	0.80	2.14	(0.42)	2.56	2.5	0
	C_6D_6	1.18	(0.87)	0.31	1.78	(0.65)	2.43	2.5	0
IIb	$CDCl_3$	1.27	(0.19)	1.08	2.29	(0.84)	3.13	3.2	0
	C_6H_6	1.08	(0.50)	0.58	1.88	(1.00)	2.88	3.2	0
IIc	$CDCl_3$	1.27	(0.20)	1.07	2.31	(0.73)	3.04	3.5	0
	C_6H_6	1.11	(0.52)	0.59	1.87	(0.75)	2.62	3.3	0
IId	$CDCl_3$	1.28	(0.24)	1.04	2.24[e]	(0.73)	2.97[e]	2.9[e]	0[e]
	C_6H_6	1.15	(0.57)	0.58	1.83	(0.75)	2.58	3.0	0
IIe	$CDCl_3$[d]	1.15	(0.03)	1.12	2.69[e]	(0.05)	2.74[e]	$J_{Pa} + J_{Pb} =$ *ca.* 16.5	
	C_6H_6[f]	0.94	(0.23)	0.69	2.38	(0.14)	2.52	~1.5[e]	14.5[e]

[a] δ is in ppm downfield from tetramethylsilane, J is in Hz. Values in parentheses represent Δ values. J_{ab} varied between 14.0 and 14.5 Hz, inclusive. [b] The ^3J values for IIa–d, unlike those in the dioxa[10] and diaza[11] analogs, are very small and are reversed in relative magnitude with respect to H_a and H_b. It could be presumed that coupling through sulfur is poor; however, IIe has typically large values. This may reflect a through-space coupling which is operative and will be discussed in a full presentation of this work. [c] See ref 15. [d] The assignment of axial and equatorial positions is tentative. [e] These parameters were used as input for the LAOCOON 3 nmr program. The computed AB spectrum agreed very well with the experimental spectrum without iteration. The AB portion of the spectrum is nearly "deceptively simple" and, thus, other coupling constants also reproduce the experimental spectrum fairly well. However, at 220 MHz the chemical shifts of H_a and H_b were separated sufficiently to allow determination of the J values given. [f] Measured at 220 MHz.

order AA′BB′KX pattern (X = phosphorus) (δ 1.91 (H_k, br t), 2.49 (H_a, distorted d of t [actually d of d]), 2.68 (H_b, distorted d of d) ppm) from which the following parameters were extracted: $J_{ab} = 13.4 \pm 0.5$ Hz, $J_{ak} = 10.5 \pm 0.5$ Hz, $J_{bk} = 1.7$–2.0 Hz, $J_{ax} = 1.5$–1.8 Hz, $J_{bx} \cong 0$ Hz. It is clear from examination of the data that the $SC_4C_5C_6S$ portion of the ring assumes an essentially rigid chair conformation[8] with the 5-*tert*-butyl group equatorial, but the data provide no definitive information regarding the configuration at phosphorus.

Evidence for the favored positioning of substituents on phosphorus was obtained from consideration of additional nmr data (Table I) for various 2-R-5,5-dimethyl derivatives IIa–e. In IIa–d the C_5 methyl resonances are well separated and of unequal height and line width with the lower field signal appearing broader (axial assignment).[9] The chemical-shift difference of the C_5 methyl groups is almost constant for R = Me, Et, and OMe (IIb–d) but not for R = Ph and *tert*-butyl (see Table I). With R = Ph (IIa) the chemical-shift difference is larger than for IIb–d, presumably because of ring current anisotropy, but again the broadened low-field signal suggests that one conformation predominated greatly over the other.

However, the situation for the R = *tert*-butyl derivative IIe is strikingly different. The chemical-shift difference between the C_5 methyl groups is small with respect to IIa–d and the methyl resonances are almost of equal height and line width. This suggests that IIe, unlike IIa–d, may be conformationally heterogeneous or at least that the conformation of the ring is quite different. The nearly identical chemical shifts of the $C_{4,6}$ protons (Table I) are also consistent with this interpretation. In addition, the condition is further supported by the values obtained for J_{Pa} and J_{Pb}. Compounds IIa–d exhibit similarity of both three-bond couplings which are quite analogous to those in *cis*-Ia (formerly denoted Ial) and consistently small ($J_{Pa} = 2.5$–3.5 Hz; $J_{Pb} \cong 0$ Hz). Placement of bulky *tert*-butyl on phosphorus causes one ^3J value to become much larger, most probably reflecting a change about the configuration at phosphorus. Taken together the above results seem best explained in terms of a similar and axial preference for the various substituents on phosphorus with the exception of the *tert*-butyl group which may experience severe syn-axial steric interactions and, hence, prefer to exist, at least partly, in an equatorial orientation or may force the ring to assume a twist conformation.[12]

Additional substantiation for the general axial preference of the P substituents in IIa–d is provided by

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(8) The nmr spectra of other derivatives, namely IIa–d (see text) and the major isomer of Ib, were also consistent with this interpretation. The nmr data will be discussed at greater length in the full paper.

(9) Such coupling through the well-documented "W" pathway has been observed in various *rigid* six-membered ring systems including 5,5-dimethyl-2-R-2-phospha-1,3-dioxa-[10] and -1,3-diaza-[11] cyclohexanes.

(10) (a) D. Gagnaire, J. B. Robert, and J. Verrier, *Bull. Soc. Chim. Fr.*, 2392 (1968); (b) D. W. White, G. K. McEwen, R. D. Bertrand, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 7125 (1970); *J. Magn. Resonance*, **4**, 123 (1971).

(11) R. O. Hutchins, D. Gagnaire, J. B. Robert, B. E. Maryanoff, J. P. Albrand, and A. Cogne, submitted for publication.

(12) As suggested by a referee, IIe was examined by low-temperature nmr in the hope of slowing any conformational changes sufficiently to observe separate resonances for different forms. Unfortunately, the results were inconclusive. The *tert*-butyl and 5-methyl signals were only slightly broadened down to −100° and no distinct separation was observed. The $C_{4,6}$ proton region broadened and the signals became complex, but no distinct pattern evolved. Solubility problems have thus far precluded study below −100° and the situation is complicated by the fact that the relative populations of more than one conformational form would be temperature dependent. The relatively small change in the methyl and *tert*-butyl resonances may suggest a predominant flexible twist conformation in which pseudorotation (which averages the signals) could be rapid even at −100° or a half-chair conformation with a planar C_4SPSC_6 region (see ref 13). In this latter conformation, the barrier to inversion of the $C_4C_5C_6$ region should also be sufficiently low to permit interchange even at −100°. Interestingly, the presence of either of these conformations requires that the chair form with equatorial *P-tert*-butyl be disfavored for some reason or that the chair–boat energy difference be low. Pertinent to this latter question is the very recent suggestion by Bentrude[14] that $-\Delta G$(chair–boat) = *ca.* 1 kcal/mol for *cis*-2,5-di-*tert*-butyl-2-phospha-1,3-dioxacyclohexan-2-one. However, the J_{PSCH} values (14.5 and *ca.* 1.5 Hz) observed for IIe are quite divergent although the average of their sum is similar to the corresponding averaged three-bond couplings in acyclic derivatives (*i.e.*, $^3J_{PSCH} =$ *ca.* 7.5 Hz in $(CH_3CH_2S)_3P$) which are presumably freely rotating. Thus, a flexible, pseudorotating twist form probably should show more nearly similar $^3J_{PSCH}$ values than obtained. Taken together the data appear more in line with a predominantly rigid chair conformation with an equatorial *P-tert*-butyl group instead of a freely rotating twist form.

(13) An X-ray analysis of *trans*-2-triphenylmethyl-4,6-dimethyl-2-phospha-1,3-dioxacyclohexan-2-one reveals a half-chair conformation with the C_4OPOC_6 region nearly coplanar: M. G. B. Drew, J. Rodger, D. White, and J. G. Verkade, *Chem. Commun.*, 227 (1971).

(14) W. G. Bentrude and D. C. Yee, *J. Chem. Soc., Chem. Commun.*, 169 (1972). Noteworthy was the finding that both $POCH_a$ and $POCH_b$ are equal (10 Hz) in *cis*-2,5-di-*tert*-butyl-2-phospha-1,3-dioxacyclohexan-2-one which is suggested to exist predominantly in a boat conformation.

observing the chemical shifts of H_a and H_b[15] in the *P*-methoxy and *P*-phenyl derivatives compared to model compounds, *i.e.*, IIc and IId. When methoxy is the P substituent (IIb), a deshielding of H_a occurs, which is in line with an axial positioning. Moreover, the presumably axial phenyl in IIa *shields* both H_a and H_b, but H_a(axial) is shielded substantially more than H_b. In fact, the shielding influence of the phenyl group is so strong that the normal order (axial at lower field) of the chemical shifts for the 4,6 proton is reversed in *cis*-Ia.[16]

Finally, compelling evidence for the above conclusions was obtained by a nuclear Overhauser effect (NOE) experiment with IIc. Irradiation of the *P*-methyl signal gave substantial enhancement (*ca.* 7%) of the axial C_4 protons. Such enhancement indicates a close proximity between the methyl and the axial protons which is possible only if the methyl group is axial.

The evidence presented here extends the scope of the preference for axiality of phosphorus substituents in six-membered rings. Such a phenomenon is probably largely a consequence of axial–axial van der Waals attractive interactions (a function of the long P–X bonds and flattening of the X–P–X portion of the ring) rather than polar bond or adjacent lone-pair interactions,[3b] since the axial preference still exists in the absence of adjacent heteroatoms.[4] A complete discussion of this and additional related work will appear at a later date.

Acknowledgment. We wish to express our gratitude to Mrs. Carol Folk (University of Pennsylvania) for the 100-MHz proton and ^{31}P nmr spectra and to Davis W. Lamson (Johnson Foundation) for obtaining 220-MHz pmr spectra. We also thank Dr. Ernest Eliel for helpful discussion and suggestions and M. Gail Hutchins for low-temperature nmr spectra.

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(15) The assignment of the axial and equatorial methylene protons in IIa–d was based on a comparison with *cis*-Ia (and *cis*-Ib) and was confirmed by double-irradiation experiments (Me_{ax} decoupled from H_a).

(16) It was observed that the axial C_4,C_6 protons in *cis*-2-phenyl-5-*tert*-butyl-2-phospha-1,3-dioxacyclohexane (the most stable isomer) resonated at higher field relative to the equatorial protons, a reversal of the usual order in these systems. This anomaly was attributed to shielding caused by the benzene ring current and was presented as evidence for the preferred axial position of the *P*-phenyl.[2]

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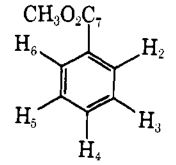
Proton Magnetic Resonance Spectrum of Methyl Benzoate-*carboxyl*-^{13}C

Sir:

A limited number of long-range ^{13}C–H coupling constants[1] have been successfully determined from natural abundance carbon-13 spectra[2a] and from the carbon-13 satellite regions of proton spectra.[2b] The former method entails the inherently difficult task of obtaining high-resolution nmr from the weak cmr spectra while the latter method involves deciphering tightly spaced carbon-13 satellites from an intense proton center band.[3] As a continuation of our nmr studies of carbon-13 enriched compounds,[4] we have determined long-range $J_{^{13}C-H}$ values of methyl benzoate-*carboxyl*-^{13}C by a detailed pmr study. In this study it was also possible to determine the relative signs of these $J_{^{13}C-H}$ values.[5]

The pmr spectrum of methyl benzoate-*carboxyl*-^{13}C was much different from the pmr spectrum of the natural abundance compound, reflecting the extensive coupling between the C-7 carbon and the various protons. Both of these spectra were analyzed by the LAOCOON-III program[6] to give the parameters listed in Table I. In this LAOCOON analysis, various combina-

Table I. Proton Magnetic Resonance Parameters for Natural and Labeled Methyl Benzoate-*carboxyl*-$^{13}C^a$



Chemical shift, δ	Natural	Labeled
H_2, H_6	8.03^b	8.03
H_3, H_5	7.40^b	7.40
H_6	7.51^b	7.52
Coupling constants, Hz		
J_{23}, J_{56}	$+7.86^b$	+7.87
J_{24}, J_{46}	$+1.30^b$	+1.33
J_{25}, J_{36}	$+0.65^b$	+0.61
J_{26}	$+1.86^b$	+1.85
J_{34}, J_{45}	$+7.45^b$	+7.50
J_{35}	$+1.35^b$	+1.33
$J_{C_7-H_2}$, $J_{C_7-H_6}$		(+) 4.08
$J_{C_7-H_3}$, $J_{C_7-H_5}$		(+) 1.11
$J_{C_7-H_4}$		(+) 0.48
J_{C_7-OCH}		3.73^c

[a] Samples run in $CDCl_3$ with a concentration of 100 mg of solute/0.5 ml of solvent with 3% TMS as an internal standard, on a JEOL PS-100 nmr spectrometer. [b] The pmr parameters for methyl benzoate have been previously determined (neat with 10% TMS) to be (K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, **25**, 422 (1968)), respectively: δ 8.05, 7.35, 7.45 (J = 7.88, 1.31, 0.61, 1.85, 7.52, 1.33 Hz). [c] Observed and measured directly from the methyl pmr region.

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(1) For references to long-range ^{13}C–H spin–spin coupling, see: (a) J. Feeney and P. J. S. Panwels, *Mol. Phys.*, **14**, 209 (1968); (b) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967); (c) S. Porcic and J. D. Roberts, *ibid.*, 87, 1056 (1965); (d) E. A. Hill and J. D. Roberts, *ibid.*, **89**, 2047 (1967); (e) A. B. Harmon and K. M. Harmon, *ibid.*, 88, 4093 (1966); (f) A. R. Tarpley, Jr., and J. H. Goldstein, *ibid.*, **93**, 3573 (1971); (g) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *ibid.*, **83**, 2778 (1961); (h) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *ibid.*, **84**, 37 (1962); (i) G. J. Karabatsos, *ibid.*, **83**, 1230 (1961); (j) G. Miyazima, Y. Utsumi, and K. Takahashi, *J. Phys. Chem.*, **73**, 1370 (1969); (k) K. M. Crecely, R. W. Crecely, and J. H. Goldstein, *ibid.*, **74**, 2680 (1970); (l) H. Dreeskamp and E. Sackmann, *Z. Phys. Chem.*, **34**, 273 (1962); (m) G. Govil, *J. Chem. Soc. A.*, 1420 (1967); (n) E. Sackmann and H Dreeskamp, *Spectrochim. Acta*, **21**, 2005 (1965); (o) A. R. Tarpley, Jr., and J. H. Goldstein, *J. Mol. Spectrosc.*, **37**, 432 (1971); (p) J. M. Read, Jr., R. E. Mayo, and J. H. Goldstein, *ibid.*, **22**, 419 (1967); (q) R. Freeman, *J. Chem. Phys.*, **43**, 3087 (1965); (r) H. Dreeskamp, K. Hildenbrand, and G. Pfisterer, *Mol. Phys.*, **17**, 429 (1969).

(2) For references to long-range ^{13}C–H spin–spin coupling in aromatic systems, (a) see ref 1b; (b) see ref 1o and 1p.

(3) Some success has been experienced in suppressing the center band so that weak satellites can be observed.[1m,1q]

(4) A. M. Ihrig and J. L. Marshall, *J. Amer. Chem. Soc.*, **94**, 1756 (1972).

(5) For examples of $J_{^{13}C-H}$ sign determinations, see ref 1b, 1k, 1o, and 1r.

(6) A. A. Bothner-By and S. M. Castellano, "Computer Programs for Chemistry," Vol. 1, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.