BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3436—3440 (1975)

An INDO Molecular-orbital Interpretation of the NMR of Several Protonated Heteroaliphatic Compounds

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(Received February 14, 1975)

Several protonated alcohols, acids, and esters were investigated by means of the INDO-MO theory and in connection with their proton and carbon-13 NMR results. The relative stability of the protonated conformers as detected by the NMR spectroscopy, had a good coincidence with the MO-theory and the experimental results. The proton or carbon-13 chemical shifts and coupling constants also showed satisfactory linear correlations between the theory and the experiment; the proton and isotropic (^{13}C) chemical shifts could be well explained by the linear correlation between the diamagnetic shielding constant and the electron density on the proton of the O–H bond and between the calculated paramagnetic shielding effect and the observed isotropic chemical shifts. The observed coupling constants of the proton and carbon-13 NMR had good overall parallelisms with those evaluated by means of the Fermi contact effect.

Considerable interest has recently centered on the elucidation of the structures of protonated heteroaliphatic compounds, with particular attention being paid to the NMR results of their protons or carbonium carbons.[1)] Concerning protonated aliphatic alcohols, acids, and esters, which were investigated in the present work, Olah *et al.* [2–7)] and others[8–10)] have extensively studied their proton or carbon-13 NMR in a superacid system and have reported that all the keto-protonated conformers except for protonated alcohols are stable species.

The protonated compounds of the above oxygenated species, however, have been the object of only limited investigation in terms of their molecular orbital treatments. Only protonated formic acid has been studied in a few *ab initio* calculations;[11–13)] the small Gaussian basis sets brought about some discrepancy between theory and experiment with respect to the relative stability of the protonated isomers.[12)]

In connection with the NMR observations of several protonated species, an extensive investigation of the protonated compounds seems significant and of interest. In the present study we will focus on the PMR or ^{13}C NMR chemical shifts and coupling constants of the protonated conformers of alcohols, acids, and esters from the viewpoints of both the INDO-MO theory and experiments.

Method of Calculation

The following five homologue series were investigated in this work: (a) the protonated formates, $HC(OH)OR^+$ (R=H, CH_3, and CH_3CH_2); (b) the protonated acetates, $CH_3C(OH)OR^+$ (R=H, CH_3, and CH_3CH_2); (c) the protonated methyl esters, $RC(OH)OCH_3^+$ (R=H, CH_3, and CH_3CH_2); (d) the protonated acids, $RC(OH)_2^+$ (R=H, CH_3, and CH_3CH_2), and (e) the protonated alcohols, ROH_2^+ (R=CH_3, CH_3CH_2, and $CH_3CH_2CH_2$).

Since the geometric data for the above protonated compounds (except $HC(OH)_2^+$) are not available in the literature, the geometries of the protonated compounds were assumed to be the same as those of the parent molecules, which can be found in a standard compendium,[14)] except for the bond lengths of C–O, R_{CO}, in $C\text{–}OH^+ = R_{CO}$ in C–OH or C–OR, $R_{OH^+} = R_{OH}$, and $\angle COH^+ = \angle COH$ or $\angle COR$; they are given in Table 1. The bond lengths of R_{CC} and R_{CH} were uniformly taken to be 1.54 Å and 1.09 Å respectively, while the bond angles of C–C–C and H–C–C were

Table 1. Assumed geometries of protonated compounds

Series	No.	Molecule	R_{CO}/Å	R_{OH}/Å	∠OCO	∠COC	∠COH
Protonated formates	1	$HC(OH)OH^+$ [a)]	1.312	0.95	124°18′		107°48′
	2	$HC(OH)OCH_3^+$	1.334	0.96	125°52′	114°47′	114°47′
	3	$HC(OH)OC_2H_5^+$	1.334	0.96	125°52′	114°47′	114°47′
Protonated acetates	4	$CH_3C(OH)OH^+$	1.430	0.95	130°		107°48′
	5	$CH_3C(OH)OCH_3^+$	1.360	0.96	124°	113°	116°
	6	$CH_3C(OH)OC_2H_5^+$	1.334	0.96	125°52′	114°47′	114°47′
Protonated methyl esters	2	$HC(OH)OCH_3^+$	1.334	0.96	125°52′	114°47′	114°47′
	5	$CH_3C(OH)OCH_3^+$	1.360	0.96	124°	113°	116°
	7	$C_2H_5C(OH)OCH_3^+$	1.360	0.96	124°	113°	114°47′
Protonated acids	1	$HC(OH)_2^+$	1.312	0.95	124°18′		107°48′
	4	$CH_3C(OH)_2^+$	1.430	0.95	130°		107°48′
	8	$C_2H_5C(OH)_2^+$	1.430	0.95	130°		107°48′
Protonated alcohols	9	$CH_3OH_2^+$	1.421	0.958			110°15′
	10	$C_2H_5OH_2^+$	1.480	0.958			110°15′
	11	$C_3H_7OH_2^+$	1.480	0.958			110°15′

a) All geometries of the protonated compounds were assumed on the basis of those for the parent molecules (see Ref. 14).

also uniformly settled to be 109°30′ for simplicity of computation.

Results and Discussion

Geometrical Aspects. We will first discuss briefly the geometries of the protonated compounds listed in Table 1; later we will consider the NMR of protonated species. It is noteworthy here with respect to the geometries of the protonated species that the C=O distance of the parent molecule is appreciably lengthened by the protonation so as to be near the single C–O bond-distance[11–13] and that the distance between the carbonyl oxygen and the proton is somewhat longer than the O–H bond length of formic acid or methyl alcohol.[12] In order to check the plausibility of the settled geometries, we compared the stretching-force constants, K_{AB}, for the C=O and O–H bonds of the parent molecules with those for the C–O and O–H bonds of the protonated compounds, using Badger's formula[18] with the parameters of Cossee and Schachtschneider[19]:

$$K_{CO} = 1.86/(R_e-0.658)^3 \qquad (1)$$

$$K_{OH} = 1.86/(R_e-1.335)^3 \qquad (2)$$

where the equilibrium distance, R_e, was based as the settled C–O or O–H bond-distance.

In regard to the parent molecules, the K_{CO} values of 9.19—11.68 mdyn/Å and the K_{OH} values of 7.69 (alcohols) —7.99 (acids) mdyn/Å seem plausible in view of the experimental values of K_{CO}=9.7—11.2 mdyn/Å[20] and of K_{OH}=7.2 (acids)—7.6 (alcohols) mdyn/Å.[20] It is also noticeable, with respect to the geometries of the parent molecules, that the dipole moments calculated by the INDO-MO method[15,16] are satisfactorily in accordance with the observed results.[17] On the other hand, the protonated compounds showed the K_{CO} values of 4.04—6.65 mdyn/Å and the K_{OH} value of 7.62 mdyn/Å. The force constants for both the protonated compounds seem somewhat too small in view of the fact that the *ab initio* calculation on the protonated formaldehyde[11] brought about the K_{CO} value of 8.11 mdyn/Å and a somewhat longer O–H bond (R_{OH}=0.985 Å) than that of methanol[21] or formic acid.[22] It is also of interest here, with respect to the property of the protonated compounds, that the calculated first-ionization potentials[23] for all the compounds in Table 1 were higher by 0.25—0.43 a.u. than those (about five-fourths of the experimental values[17]) for their parent molecules. This trend may be explained well by the decrease in the electron densities on the oxygen lone-pair orbitals by the protonation, which causes a lowering of the highest-occupied MO localized by the said lone-pairs.

With regard to the relative stability of the keto-protonated conformers (detected by the NMR spectroscopy) of the formates, acetates, methyl esters, and acids in Fig. 1, the present INDO calculations gave a good parallelism of the stability with the NMR observations:[1,4,9,10] that is, I>II>III in the protonated formates, I>II in the protonated methyl ester, and I>II in the protonated acids. It may be deduced, therefore, that the present assumed geometries for the protonated compounds can be useful for discussing the NMR observations which will be developed below.

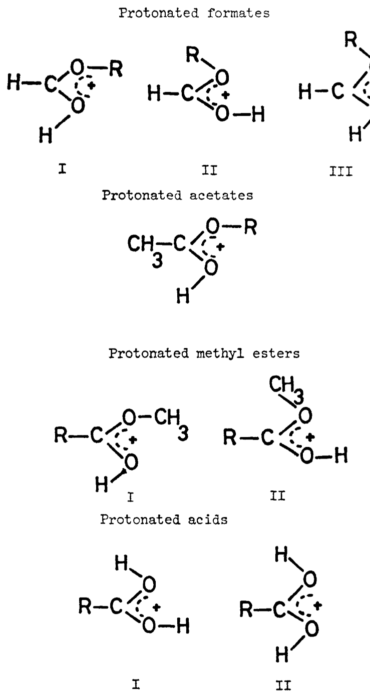

Fig. 1. Keto-protonated conformers used for the INDO calculation.

Proton Chemical Shifts and Coupling Constants. We will now investigate the correlation between the magnitude of the proton-chemical shift, δ ppm, of the protonated species and the electron density on their protons, q_H. As is shown in Fig. 2, there exist sufficient linear-correlations between the δ and q_H values for the proton of the O–H bond in all the homologue series investigated. Hence, in the proton-chemical shifts of the protonated compounds, the paramagnetic term, σ_p, and the magnetic anisotropy of the neighboring atom, σ', can be omitted from the total shielding constant, $\sigma(=\sigma_d+\sigma_p+\sigma')$, as is usual.[24] The above correlations can, then, be represented by:

$$\sigma_d(\text{ppm}) = -Aq_H \quad (A\text{: constant}) \qquad (3)$$

where σ_d denotes the diamagnetic shielding constant. It is noteworthy here that the chemical shifts of the protons in the alkyl substituent, *R*, also have a good overall parallelism with their electron densities (q_H), as is shown in Fig. 3.

Next, let us notice the coupling constants of $J_{HH'}$, with a particular view to the correlation between the experimental and calculated constants (abbreviated as $J_{HH'}^{\text{exptl}}$ and $J_{HH'}^{\text{calcd}}$ respectively). Since the proton-coupling constant depends predominantly on the Fermi-type contribution,[25] the $J_{HH'}^{\text{calcd}}$ values were evaluated by means of the following Fermi contact effect:[26]

$$J_{HH'}^{\text{calcd}} = (\hbar/2\pi)(64\pi^2/9)r_H r_{H'}\beta^2(s_H|\delta(r_H)|s_H) \times (s_{H'}|\delta(r_{H'})|(s_{H'}) \times \pi_{s_{H'}s_{H'}} \qquad (4a)$$

$$\pi_{s_{H'}s_H} = 4\sum_{i}^{\text{occ}}\sum_{j}^{\text{unocc}}(\varepsilon_i-\varepsilon_j)^{-1}c_{is_H}c_{is_{H'}}c_{js_H}c_{js_{H'}} \qquad (4b)$$

where the notations have the same meanings as in

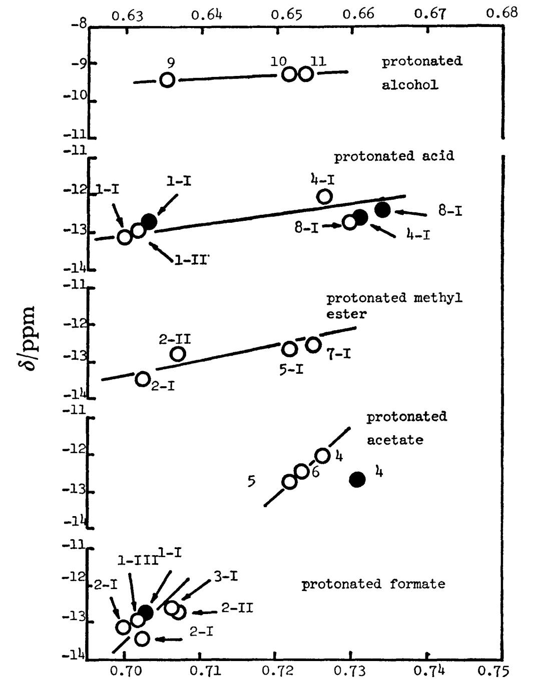

Fig. 2. Plots of δ *vs.* q_H values (remarked signs are specified in Table 1 and Fig. 1: empty circle for *cis*-proton against R; filled circle for *trans*-proton against R).

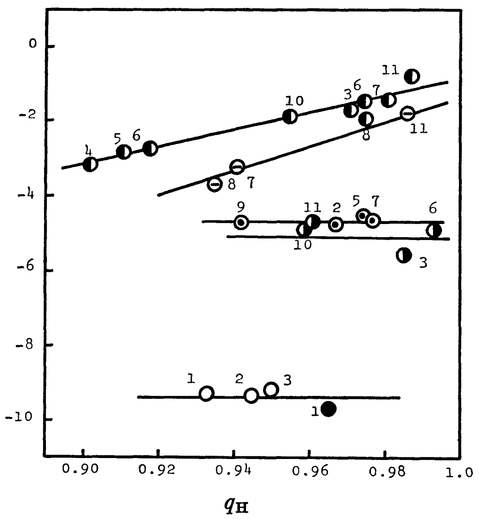

Fig. 3. The correlations between the δ values for the protons on the alkyl substituents and the q_H values (all compounds except the *cis-cis* isomer indicated by a filled circle, are the *cis-trans* protonated species specified by the compound number in Table 1).
○ or ●: H(-C); ⊖: CH_2(-C); ◑: CH_2(-O)
◐: CH_3($-CH_2$); ⊙: CH_3(-O).

Ref. 26; the atomic orbital constants and the nuclear magnetogyric ratio (r_H or $r_{H'}$) were taken to be 0.5500 a.u.[27] and 2.675×10^4 $G^{-1}s^{-1}$ respectively. The $J_{HH'}^{calcd}$ and $J_{HH'}^{exptl}$ values for the protonated formic acid and methyl formate are plotted against one another in Fig. 4 (the other protonated compounds in Table 1 were not found in the NMR data). The correlation

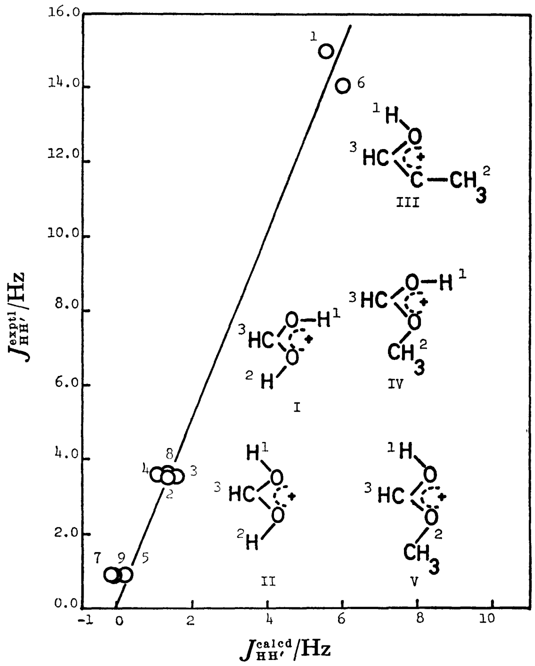

Fig. 4. Plots of $J_{HH'}^{exptl}$ *vs.* $J_{HH'}^{calcd}$ values.
1: J_{13}(I) 2: J_{23}(I) 3: J_{13}(II)$=J_{23}$(II) 4: J_{13}(III) 5: J_{23}(III) 6: J_{13}(IV) 7: J_{23}(IV) 8: J_{13}(V) 9: J_{23}(V).

can be shown by a straight line with an intersect of zero, but the slope of the straight line was not 45°.

Carbon-13 Chemical Shifts and Coupling Constants. We will now investigate the correlations between the calculated and observed ^{13}C-chemical shifts and coupling constants, using the ^{13}C NMR (data found only for the protonated acids) and INDO calculation results. In the calculation, the total shielding tensor, σ, was approximated by the paramagnetic shielding effect, σ_p^{AA}, without the diamagnetic contribution and the effects of the circulation on all the other atoms and of ring currents:[28]

$$\sigma_p^{AA} = ((\sigma_p)_{xx} + (\sigma_p)_{yy} + (\sigma_p)_{zz})/3 \tag{5a}$$

$$(\sigma_p)_{zz} = -(e^2\hbar^2/2m^2c^2(\Delta E))\langle r^{-3}\rangle_{2p}[(Q_{AA})_{zz}+\sum_{AB}(Q_{AB})_{zz}] \tag{5b}$$

$$(Q_{AA})_{zz} = 2-2(P_{x_Ax_A}-1)(P_{y_Ay_A}-1) + 2P_{x_Ay_A}{}^2 \tag{5c}$$

$$(Q_{AB})_{zz} = -2P_{x_Ax_B}P_{y_Ay_B} + 2P_{x_Ay_B}P_{y_Ax_B} \tag{5d}$$

where $(\sigma_p)_{xx}$ and $(\sigma_p)_{yy}$ can be given by corresponding terms and where the notations have the same meanings as in Ref. 28. The calculated and observed ^{13}C -chemical shifts (δ_{calcd} and δ_{obsd} respectively) from the reference substance of carbon disulfide are listed in Table 2. In Table 2, the average excitation energy (ΔE) for the protonated species was taken to be a number (7.9 eV) higher than that for the parent molecules (ΔE=7.7 eV), because the energies of the ground states in the former were appreciably lower than those in the latter, and because the energies of the excited states in the former were slightly higher than those in the latter. As can be seen from Table 2, there is a good overall agreement of the δ_{calcd} values with the δ_{obsd} values, and the ^{13}C-chemical shifts of

TABLE 2. CALCULATED AND OBSERVED ISOTOROPIC (^{13}C)-CHEMICAL SHIFTS EOR SOME PROTONATED AND PARENT MOLECULES

Molecule	ΔE/eV	$-\sigma_{\text{p}}^{\text{AA}}$/ppm	δ_{calcd}/ppm	δ_{exptl}/ppm
$H^{13}COOH$	7.7	359.5	34.5	27.0$^{a)}$
$H^{13}C(OH)_2^+$(*cis-trans*)	7.9	382.8	20.9	17.0$^{a)}$
$H^{13}C(OH)_2^+$(*cis-cis*)	7.9	382.1	21.5	19.9$^{a)}$
$CH_3{}^{13}COOH$	7.7	375.1	18.9	15.6$^{a)}$
$CH_3{}^{13}C(OH)_2^+$	7.9	413.5	−9.1	−1.6$^{b)}$
$CH_3CH_2{}^{13}COOH$	7.7	375.0	19.0	14.8$^{a)}$
$CH_3CH_2{}^{13}C(OH)_2^+$	7.9	413.3	−8.8	1.6$^{a)}$
$CH_2{}^{13}COOCH_3$	7.7	374.8	19.2	23.0$^{c)}$
$CH_2{}^{13}C(OH)OCH_3^+$	7.9	393.7	0.3	
$CH_3{}^{13}COOC_2H_5$	7.7	372.8	21.2	22.9$^{c)}$
$CH_3{}^{13}C(OH)OC_2H_5^+$	7.9	390.6	3.4	
$CH_3{}^{13}COOCH_2\cdot CH_2CH_3$	7.7	373.0	21.0	22.3$^{c)}$
$CH_3{}^{13}C(OH)OCH_2\cdot CH_2CH_3^+$	7.9	390.4	3.6	
$H^{13}COOCH_2CH_3$	7.7	353.3	40.7	33.0$^{c)}$
$H^{13}C(OH)OCH_2CH_3^+$	7.9	370.3	23.7	
$^{13}CS_2$	7$^{d)}$	394.0$^{d)}$	(0)	0

a) From Ref. 6. b) From Ref. 7. c) From J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964). d) From Ref. 29.

the protonated compounds appeared in a lower magnetic field than those of the parent molecules. It is of interest here to notice the changes in the local isotropic chemical shifts ($(\sigma_{\text{p}})_{xx}$, $(\sigma_{\text{p}})_{yy}$, and $(\sigma_{\text{p}})_{zz}$) due to the protonation, taking the formic acid and its protonated species (all the atoms on the *x*-*y* cross section and the C=O and C$^+$–OH bonds on the *y* axis) as examples. The *yy* element, $(\sigma_{\text{p}})_{yy}$, is deshielded predominantly by the protonation from −243 ppm to about −340 ppm; the *xx* element is shielded by about 32 ppm (from −459 ppm), while the *zz* element is deshielded slightly by about −2 ppm (from −378 ppm). In this case, all the elements (*xx*, *yy*, and *zz*) of the *cis-trans* isomer, I, are not markedly different from those of the *cis-cis* isomer, III. The negative *yy* element of the multiple-bond terms $(\sum_{B\neq A} Q_{AB})$ for the protonated molecule is appreciably diminished by the protonation to be less than one half of that for the parent compound.

TABLE 3. CALCULATED AND OBSERVED C^{13}-NMR COUPLING CONSTANTS AND %S CHARACTER FOR PROTONATED AND PARENT MOLECULES

Molecule	$J^{\text{exptl}}_{^{13}\text{CH}}$/Hz	$J^{\text{calcd}}_{^{13}\text{CH}}$/Hz	%s	Hybridization
$HC^{13}OOH$	225.1$^{a)}$	75.91	29.74	$sp^{2.36}$
$HC^{13}(OH)_2^+\cdot$ (*cis-trans*)	244.8	83.98	31.68	$sp^{2.16}$
$HC^{13}(OH)_2^+\cdot$ (*cis-cis*)	235.8$^{a)}$	82.06	31.59	$sp^{2.17}$
$HC^{13}OOCH_3$	226.2$^{b)}$	76.03	29.65	$sp^{2.37}$
$HC^{13}OOCH_2CH_3$	225.6$^{b)}$	75.47	29.65	$sp^{2.37}$

a) From Ref. 6. b) From N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).

Finally, we will discuss the carbon-13 NMR coupling constants, $J^{13}{}_{\text{CH}}$, of the protonated compounds. The $J^{13}{}_{\text{CH}}$ values were calculated by means of equations similar to Eqs. (4a—4b), with the $r^{13}{}_{\text{C}}$ value of $0.6726\times 10^4\ \text{G}^{-1}\text{s}^{-1}$ and the carbon atomic orbital constant of 2.767.[27] In Table 3 we list the calculated and experimental $J^{13}{}_{\text{CH}}$ values (denoted as $J^{\text{calcd}}_{^{13}\text{CH}}$ and $J^{\text{exptl}}_{^{13}\text{CH}}$ respectively) and the %s characters for the protonated formic acid and a few parent molecules. Here, the %s character was evaluated from the INDO-MO calculation results, with the following relation:

$$\%\text{s} = 100N_{\text{C}_\text{s}}/(N_{\text{C}_\text{s}}+N_{\text{C}_\text{p}}) \tag{6}$$

where N_{C_s} and N_{C_p} stand for the AO densities of the carbon-13 s- and p-orbitals respectively.

There is a satisfactorily good linear correlation between the $J^{13}{}_{\text{CH}}$ values and the %s characters; this correlation can be expressed by:

$$J^{\text{exptl}}_{^{13}\text{CH}} = 7.25\%\text{s} + 14.99 \quad \text{(in Hz unit)} \tag{7a}$$

$$J^{\text{calcd}}_{^{13}\text{CH}} = 3.66\%\text{s} - 32.03 \quad \text{(in Hz unit)} \tag{7b}$$

The contribution of the %s character to the isotropic chemical shifts is different between the calculated and the experimental results, so this is reflected in the slope (not unity) of the linear correlation between the $J^{\text{exptl}}_{\text{C}^{13}\text{H}}$ and $J^{\text{calcd}}_{\text{C}^{13}\text{H}}$ values:

$$J^{\text{exptl}}_{^{13}\text{CH}} = 2.16J^{\text{calcd}}_{^{13}\text{CH}} + 61.4 \quad \text{(in Hz unit)} \tag{8}$$

The trend shown in Eqs. (7a—b and 8) may be attributed mainly to the gap between the conditions in the present calculation and those in the NMR experiment; it seems that the %s character is not completely correct in view of the approximations involved in the INDO-MO theory.

The calculations were carried out on a FACOM 230-75 computer at the Data Procession Center of Kyushu University.

References

1) The protonated heteroaliphatic compounds have been reviewed by G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).

2) G. A. Olah and E. Namanworth, *J. Amer. Chem. Soc.*, **88**, 5327 (1966).

3) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

4) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

5) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid* **89**, 5694 (1967).

6) G. A. Olah and A. M. White, *ibid.*, **89**, 7072 (1967).

7) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

8) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).

9) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. Maclean, *Chem. Comm.*, 898 (1966).

10) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967).

11) P. Ros, *J. Chem. Phys.*, **49**, 4902 (1968).

12) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *ibid.*, **52**, 1784 (1970).

13) A. C. Hopkinson and I. G. Csizmadia, *Can. J. Chem.*, **52**, 546 (1974).

14) L. E. Sutton, Editor, "Tables of Interatomic Distances," The Chemical Society, London, Special Publications No. 11 (1958) and No. 18.

15) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N, Y. (1970).

16) M. D. Newton, W. A. Lathan, W. J. Hegre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

17) K. Ohkubo, K. Tsuchihashi, and M. Okada, This Bulletin, in press.

18) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

19) P. Cossee and J. H. Schachtschneider, *ibid.*, **44**, 97 (1966).

20) W. V. F. Brooks and C. M. Haas, *J. Phys. Chem.*, **71**, 650 (1967).

21) E. U. Ivash and D. M. Denison, *J. Chem. Phys.*, **21**, 1804 (1953).

22) I. L. Karle and J. Karle, *ibid.*, **22**, 43 (1954).

23) The first ionization potentials were obtained from the energy of the highest-occupied MO as a positive number, according to the Koopmans theorem (T. Koopmans, *Physica*, **1**, 104 (1933)).

24) T. Yonezawa, H. Kato, H. Saito, and K. Fukui, This Bulletin, **35**, 1814 (1962).

25) H. M. McConnel, *J. Chem. Phys.*, 23, 760 (1955); **24**, 460 (1956).

26) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

27) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, National Physical Laboratory Report BPR13 (1962).

28) J. A. Pople, *Mol. Phys.*, **7**, 301 (1964).