salt and lithium or cesium salts, it was not possible to measure directly the pK of FD in either LiCHA–CHA or CsCHA–CHA.

The results in LiCHA–CHA and other solvent systems are summarized in Table VI. The relative acidity between BPP and BBP, or between FD and DPI, is nearly the same in all of the solvent systems we have studied. For example, FD is more acidic than DPI by 1.77 pK units in CHA, an ion pair system, quite close to the 1.6 pK unit difference in DMSO or for ionic equilibria in $NaOCH_3$–CH_3OH.[23]

However, BPP is more acidic than DPI by 0.66 pK unit in CsCHA–CHA, 1.71 units in LiCHA–CHA, and 1.97 units in DMSO; BBP is more acidic than DPI by 0.15 pK unit in CsCHA–CHA, 1.12 units in LiCHA–CHA, and 1.31 units in DMSO. The general similarity of the relative pK's in CsCHA–CHA and in CHA itself where available further suggests that the cyclohexylammonium carbanide ion pairs involved in CHA are of the contact type. The results for LiCHA–CHA accord completely with the predictions of the electrostatic treatment. This set of results provides further emphasis of the care required in the use of relative acidities when ion pairs are involved; however, it is also clear that changes in relative acidities are frequently understandable from straightforward considerations of solvation and electrostatic interactions. The present results, for example, completely confirm the applicability of simple electrostatic concepts as developed in the preceding paper.[17]

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(23) A. Streitwieser, Jr., C. J. Chang, and A. T. Young, Jr., *J. Amer. Chem. Soc.*, in press (paper XXXIX).

Ground States of σ-Bonded Molecules. XVII.[1] Fluorine Compounds[2]

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Abstract: MINDO/2 has been extended to compounds containing carbon, hydrogen, and fluorine, using an improved scheme, based on Oleari's method for the one-center integrals. The calculated heats of formation, molecular geometries, dipole moments, and ionization potentials agree well with experiment. The calculations cover *ca.* 90% of molecules for which reasonably reliable experimental data are available.

Previous papers of this series[1,4,5] have described a semiempirical SCF all-valence-electron MO treatment of ground states of molecules, the parameters being chosen to optimize calculated heats of formation and molecular geometries. The treatment involves two numerical parameters per atom pair; values for these were determined for molecules derived from carbon, hydrogen, nitrogen, and oxygen. Here we describe an extension of MINDO/2 to compounds containing carbon, hydrogen, and fluorine. Parameters for the pairs NF and OF have not yet been determined because there is a dearth of thermochemical data for compounds containing them.

Preliminary attempts to extend MINDO/2 to fluorine were not very satisfactory. We eventually became convinced that these difficulties were consequences of another failing of MINDO/2, its overestimation of dipole moments by *ca.* 50%. The corresponding errors in calculated charge distributions seemed likely to cause peculiar difficulties in compounds containing fluorine since the charges in them are especially large. We have now found that the calculation of dipole moments can be improved by abandoning the simplifying assumptions previously made in MINDO/2 in the estimation of one-center integrals and these changes did indeed solve the fluorine problem as well. Since the changes do not alter the results of MINDO/2 calculations in any other respect, they seem to represent a worthwhile advance. While only compounds containing C, H, and F are discussed in this paper, parameters are also given for C, H, O, and N.

Theoretical Procedure. In the MINDO method,[6] none of the one-center integrals are neglected. There are therefore eight such integrals to be determined for atoms in their valence states, *viz.*

$$U_{ss},\ U_{pp},\ g_{ss},\ g_{sp},\ g_{pp},\ g_{pp'},\ h_{sp},\ h_{pp'} \tag{1}$$

where

$$g_{\mu\nu} = (\mu\mu,\nu\nu);\quad h_{\mu\nu} = (\mu\nu,\mu\nu) \tag{2}$$

In MINDO/1[6] and MINDO/2[4] these are determined from the Slater–Condon parameters as follows:

$$g_{ss} = g_{sp} = F^0;\ g_{pp} = F^0 + 4/25F^2;\ g_{pp'} = F^0 - 2/25F^2;\ h_{sp} = 1/3G^1;\ h_{pp'} = 3/25F^2 \tag{3}$$

The values for F^2 and G^1 were those used also by Pople,

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(1) Part XVI: M. J. S. Dewar and M. C. Kohn, *J. Amer. Chem. Soc.*, **94**, 2704 (1972).

(2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-70-C-0121 and the Robert A. Welch Foundation through Grant F-126.

(3) Robert A. Welch Postdoctoral Fellow.

(4) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(5) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

(6) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, 50, 1262 (1969).

et al.,[7] in their INDO approximation. U_{ss}, U_{pp}, and F^0 were found by fitting the differences in energy between the high-spin configuration ($s^m p^n$) of the atom in its ground state and corresponding high-spin configurations $s^m p^{n-1}$, $s^m p^{n+1}$, and $s^{m-1} p^{n+1}$.

In order to use this scheme one is forced to assume that g_{ss} and g_{sp} are equal (eq 3). This is consistent with the assumption that the two-center repulsion integral has a common value γ_{AB} for any AO of atom A and any AO of atom B, depending only on the internuclear distance R_{AB}, for in the limit when R_{AB} tends to zero, γ_{AB} can tend to g_{ss} or g_{sp}. On the other hand this argument would equally require g_{ss}, g_{sp}, g_{pp}, and $g_{pp'}$ to be equal and these additional assumptions were indeed made in the PNDO approximation.[8] The assumption that g_{ss} and g_{sp} have a common value, but one different from that of g_{pp} or $g_{pp'}$, is therefore not really justifiable and our studies suggest that this assumption is to a certain extent responsible for the poor values of dipole moments given by the original version of MINDO/2.

Oleari and his collaborators[9] have suggested an alternative scheme for determining the one-center integrals (4), by a least squares fit to the *total* valence state energies (E_A) of the atom as a function of its orbital occupation number n_μ. It can be shown that

$$E_A = \sum_\mu n_\mu U_{\mu\mu} + {}^1\!/_2 \sum_\mu \sum_{\nu \neq \mu} n_\mu n_\nu g'_{\mu\nu} + {}^1\!/_2 \sum_\mu n_\mu (n_\mu - 1) g_{\mu\mu} \quad (4)$$

where

$$g'_{\mu\nu} = g_{\mu\nu} - {}^1\!/_2 h_{\mu\nu} \quad (5)$$

In this way they obtained values for the quantities U_{ss}, U_{pp}, g_{ss}, g_{pp}, g'_{sp} and $g'_{pp'}$ for the second and third row elements.

Oleari, *et al.*, based their calculations on the valence state energies estimated by Skinner and Pritchard.[10]

Sichel and Whitehead[11] have repeated these calculations using the more recent estimates of valence state energies of Hinze and Jaffé.[12] There are, however, certain anomalies in the values obtained in this way which have been pointed out by Boyd and Whitehead.[13] Thus the values for g_{ss} do not change smoothly with increasing atomic number, the value for oxygen being very obviously out of step. Oleari's integrals do not suffer from this defect. One might remark that it seems strange that the values of Sichel and Whitehead should be inferior in this respect given that they are based on more recent and reputedly "better" estimates of promotion energies. An analysis of this discrepancy could prove rewarding but it does not concern us here.

Boyd and Whitehead[13] have suggested an alternative approach based on *ab initio* SCF calculations. Their results did not, however, seem relevant to us in the present connection for three reasons. First, they gave no values for the exchange integrals $h_{\mu\nu}$ since they were interested only in parametrizing the CNDO/2 method. Secondly, the number of elements for which the necessary SCF calculations are available is very limited, several elements of vital importance to us being omitted, in particular boron and aluminum. And thirdly, the values derived by Boyd and Whitehead are in fact very close indeed to those of Oleari (which are not quoted in their paper). Since the rather drastic change in one-center integrals from the original MINDO set to those used here leads, as we shall see, only to quite minor changes in the results, it is extremely unlikely that the results using the Boyd–Whitehead integrals would be detectably different from those using the Oleari ones.

We have carried out calculations using three sets of values for the one-center parameters: (a) those of Oleari, *et al.*; (b) those of Sichel and Whitehead; (c) a third set derived from those of Sichel and Whitehead by smoothing out plots of the integral *vs.* atomic number. The results using the first set, *i.e.*, that of Oleari, *et al.*, were in better agreement with experiment and we have therefore adopted them.

Oleari's analysis gives only the six parameters U_{ss}, U_{pp}, g_{ss}, g_{pp}, g'_{sp}, $g'_{pp'}$. In order to determine the individual integrals (eq 1) one must resolve g'_{sp} and $g'_{pp'}$ into their components (eq 5). The resolution of $g'_{pp'}$ is carried out using the theoretical relationships of eq 3 together with Oleari's values

$$g_{pp'} = {}^4\!/_5 g'_{pp'} + {}^1\!/_5 g_{pp}; \quad h_{pp'} = {}^2\!/_5 (g_{pp} - g'_{pp'}) \quad (6)$$

The resolution of $g_{sp'}$ is effected by using Slater's value for G^1

$$h_{sp} = {}^1\!/_3 G^1; \quad g_{sp} = g'_{sp} + {}^1\!/_6 G^1 \quad (7)$$

These resolutions of g'_{sp} and $g'_{pp'}$ can be justified in two ways.

First, the integrals $g_{\mu\nu}$ and $h_{\mu\nu}$ appear in the diagonal elements of the F matrix only as the unresolved combination $g'_{\mu\nu}$. Any error in the resolution therefore appears only in the one-center off-diagonal elements $F_{\mu\nu}{}^{AA}$ which can be written (*cf.* ref 6)

$$F_{\mu\nu}{}^{AA} = P_{\mu\nu}({}^3\!/_2 h_{\mu\nu} - {}^1\!/_2 g_{\mu\nu}) \quad (8)$$

Since the total electronic energy (E_{el}) is given by

$$E_{el} = \sum_{\mu \neq \nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \quad (9)$$

the contribution to the total electronic energy by the off-diagonal term $F_{\mu\nu}{}^{AA}$ is of the order $p_{\mu\nu}{}^2$. Since these one-center bond orders are generally small,[14] any error in E_{el} due to errors in the resolution of g'_{sp} or $g'_{pp'}$ is likely to be negligible.

Secondly, as a further check, the following calculations were carried out. Using STOs, the one-center repulsion integrals can be evaluated explicitly

$$g_{ss} = 9.8849\zeta_{2s}; \quad g_{pp} = 10.6020\zeta_{2p} \quad (10)$$

Using Oleari's values for g_{ss} and g_{pp} we can find the corresponding Slater exponents ζ_{2s} and ζ_{2p}. These exponents were then used in a theoretical evaluation of the integrals $g_{pp'}$, $h_{pp'}$, g_{sp}, and h_{sp}. The values found in this way differed by less than 2% from those estimated

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[7] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

[8] M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89**, 3089 (1967).

[9] L. Oleari, L. DiSipio, and G. De Michelis, *Mol. Phys.*, 10, 97 (1966).

[10] H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

[11] J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **7**, 32 (1967).

[12] J. Hinze and H. G. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1963).

[13] R. J. Boyd and M. A. Whitehead, *J. Chem. Soc. A*, 2469 (1970).

[14] Thus for carbon, writing the $2p_x$, $2p_y$, and $2p_z$ AOs as *x*, *y*, and *z*, respectively, and the 2s AO as s, $P_{sx} = 0.125$; $P_{sy} = 0.001$; $P_{sz} = 0.005$; $P_{xy} = 0.000$; $P_{yz} = 0.004$; $P_{xz} = 0.001$.

Table I. Atomic Parameters

	U_{ss}	U_{pp}	g_{ss}	g_{pp}	g_{sp}	$g_{pp'}$	h_{sp}	$h_{pp'}$	E_A	ζ	I_s	I_p
H	−13.595		12.848						−13.595	1.1	−13.595	
C	−52.89	−40.28	12.23	11.08	11.47	9.84	2.43	0.62	−123.50	1.625	−21.34	−11.54
N	−71.86	−57.10	13.59	12.98	12.66	11.59	3.14	0.70	−201.17	1.95	−27.51	−14.34
O	−97.83	−77.97	15.42	14.52	14.48	12.98	3.94	0.77	−314.54	2.275	−35.50	−17.91
F	−130.96	−105.03	16.92	16.71	17.25	14.91	4.83	0.90	−472.75	2.40	−43.70	−20.89

from eq 6 and 7, indicating that the latter are internally self-consistent.

A further advantage of the Oleari method is that the repulsion integrals are derived from a least-squares fit to the energies both of the neutral atom and of ions derived from it; the values found by this procedure should automatically allow for the effects of orbital contraction or expansion in ions and so be as applicable to calculations for molecular ions as for neutral molecules. The final values for the second row elements C–F are listed in Table I.

The calculated heats of atomization and geometries of molecules are relatively insensitive to U_{ss} and U_{pp}; this, however, is not the case for ionization potentials or dipole moments. These parameters are moreover likely to be the most affected by changes in the effective nuclear charge of atoms when they combine to form molecules. We have therefore made small adjustments to Oleari's values for U_{ss} and U_{pp} to give the best fit to observed dipole moments and ionization potentials. These values are also listed in Table I.

The remaining parameters were found in the same way as in the original version of MINDO/2.

The two-center repulsion integrals γ_{AB} are given by the Ohno–Klopman[15] relation

$$\gamma_{AB}(\mathrm{eV}) = 14.399[R_{AB}^2 + (\rho_A + \rho_B)^2]^{-1/2} \quad (11)$$

where

$$\rho_A = 7.1995/F_A{}^0; \; \rho_B = 7.1995/F_B{}^0 \quad (12)$$

Since F^0 does not appear directly in the present scheme, the corresponding values are chosen as an average of the 16 specific one-center interactions

$$F_A{}^0 = {}^1/_{16}(g_{ss} + 6g'_{sp} + 3g_{pp} + 6g'_{pp'}) \quad (13)$$

The core resonance integral ($\beta_{\mu\nu}{}^c$) is given by the Mulliken approximation

$$\beta_{\mu\nu}{}^c = B_{AB}(I_\mu + I_\nu)S_{\mu\nu} \quad (14)$$

where I_μ, I_ν are the valence state ionization potentials of AOs μ and ν, $S_{\mu\nu}$ is the corresponding overlap integral, and B_{AB} is a parameter characteristic of the atom pair A–B.

The core–core repulsion function CR_{AB} between atoms A and B has the form suggested by Dewar and Klopman

$$CR_{AB} = Z_AZ_B[\gamma_{AB} + (14.399/R_{AB} - \gamma_{AB})e^{-\alpha_{AB}R_{AB}}] \quad (15)$$

where R_{AB} is the internuclear distance and α_{AB} another parameter characteristic of the atom pair A–B.

The values of the parameters B_{AB} and α_{AB} were found as before[4,5] by a least-squares fit to the observed heats of atomization and bond lengths in a set of standard compounds. For the combination CHF, the compounds chosen were CH_3F, CH_2F_2, CHF_3, CH_3–CHF_2, CF_3–CF_3, $CH_2{=}CF_2$, PhF, HF, and F_2. The resulting parameters are shown in Table II. We have also redetermined the parameters for atom pairs from the set CHON, corresponding to the new set of one-center integrals (Table I). These are also listed in Table II. Here, as in the original version[4,5] of MINDO/2, systematic offsets of +0.1, +0.1, and +0.15 Å were imposed on the lengths of CH, NH, and OH bonds, respectively.

Table II. Values of B_{AB} and α_{AB} for Various Pairs of Atoms

AB	B_{AB}	α_{AB}	AB	B_{AB}	α_{AB}
HH	0.4174	0.9319	CO	0.4047	1.9827
HC	0.3356	1.2002	CF	0.3989	1.9324
HN	0.3848	1.2895	NN	0.7377	0.7683
HO	0.5195	0.9699	NO	0.3583	2.4235
HF	0.4143	1.8435	OO	0.5396	1.7720
CC	0.3327	1.7919	FF	0.3556	2.4455
CN	0.3453	1.9328			

Calculations using these parameters for compounds derived from C, H, O, and N give heats of atomization and bond lengths that are very similar to those resulting from the original[5] MINDO/2 treatment, the average errors being ±3 kcal/mol and ±0.01 Å, respectively. The error in the dipole moment however is reduced from *ca.* 50% (~1 D) to *ca.* 20% (⩽0.4 D).

The empirical adjustment of U_{ss} and U_{pp} has some justification in that the optimum Slater exponents for AOs in LCAO treatments of molecules differ from those for isolated atoms. The AOs in molecules are generally smaller. This in turn means that in calculating dipole moments of molecules, one should use for integrals of the type $\langle s|x|p_x\rangle$ values smaller than those calculated from Slater AO's using atomic Slater exponents. Following this reasoning we tried reducing the atomic dipole moment integrals by a fixed factor. In this way the error was further reduced to ±0.2 D. The final expression used to calculate dipole moments is

$$\mu_x = 4.803\sum_A(Z_A - P_{AA})x_A - 4.2\sum_A P_{sp_x}/\zeta_A \quad (16)$$

It should be noted that only small changes are needed in the MINDO/2 program to adapt it to the new parameters, the changes being confined to the block data section.[16]

Results and Discussion

A. Heats of Formation. Table III compares calculated and observed heats of formation and molecular

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(15) K. Ohno, *Theor. Chim. Acta*, 2, 219 (1964); G. Klopman, *J. Amer. Chem. Soc.*, 86, 4550 (1964); 87, 3300 (1965).

(16) This program has not yet been deposited with QCPE but copies are available on request.

Table III. Calculated and Observed Heats of Formation and Molecular Geometries for Fluorine Compounds

	Compound	Heats of formation, kcal/mol at 25°C: Calcd[a] A	Calcd[b] B	Obsd	C–F bond lengths, Å Calcd (Obsd)
1.	CH_3F	−60.8	−63.1	−67.0[c]	1.336 (1.385[v])
2.	CH_2F_2	−113.1	−114.3	−107.2[d]	1.328 (1.360[w])
3.	CHF_3	−170.2	−170.4	−165.0[d]	1.327 (1.332[x])
4.	CF_4	−226.9	−227.1	−220.5[d]	1.326 (1.317[y])
5.	CH_3CHF_2	−120.4	−120.5	−121.0[d]	1.350 (1.345[l])
6.	CH_2FCHF_2	−163.3	−163.7	−159.5[e]	1.341 (1.345[t])
7.	CH_3CF_3	−176.3	−176.7	−176.0[c]	1.339 (1.335[s])
8.	CF_3CF_3	−309.8	−310.6	−310.0[c]	1.342 (1.330[m])
9.	$CH_2FCH_2CH_3$	−72.6	−72.9	−66.8[f]	1.336
10.	CH_3CHFCH_3	−74.4	−74.4	−68.6[f]	1.344
11.	$CF_3CH_2CH_3$	−179.5	−181.3	−191.0[c]	1.340
12.	$CF_3CF_2CF_3$	−392.4	−406.3	−411.0[c]	1.340
13.	$CH_2{=}CHF$	−28.5	−31.6	−28.0[c]	1.317 (1.320[u])
14.	$CH_2{=}CF_2$	−76.6	−83.0	−78.6[c]	1.317 (1.323[n])
15.	$CHF{=}CF_2$	−115.8	−119.6	−115.1[g]	1.316
16.	$CF_2{=}CF_2$	−158.7	−160.4	−155.5[c]	1.317 (1.313[o])
17.	$CH_2{=}CHCF_3$	−142.4	−144.7	−154.0[c]	1.341
18.	Fluorobenzene	−25.2	−25.5	−26.5[c]	1.333 (1.354[p])
19.	*o*-Difluorobenzene	−67.7	−68.1	−67.7[c]	1.331 (1.350[q])
20.	*m*-Difluorobenzene	−71.2	−72.0	−71.4[c]	1.326 (1.350[r])
21.	*p*-Difluorobenzene	−69.8	−70.3	−70.7[c]	1.330 (1.350[q])
22.	Hexafluorobenzene	−229.1	−229.8	−224.0[h]	1.323
23.	Trifluoromethylbenzene	−140.7	−141.1	−140.7[i]	1.338
24.	*p*-Fluorotoluene	−35.9	−36.4	−34.6[j]	1.329
25.	*m*-Fluorotoluene	−36.8	−37.3	−33.0[k]	1.335
26.	*o*-Fluorotoluene	−36.0	−36.4	−33.0[k]	1.318

[a] Value using experimental geometry when available. When not available, the geometry was calculated using "standard" bond lengths; C–C, 1.53 Å; C–F, 1.34 Å; C–C (aromatic), 1.40 Å; C–H, 1.20 Å (including the 0.1 Å offset[4,5]). [b] Value using theoretical (SIMPLEX) geometry. [c] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, Y. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. [d] "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1965. [e] A. S. Rodgers, *J. Phys. Chem.*, **71**, 1996 (1967). [f] J. R. Lacher, A. Kranpour, and J. D. Park, *ibid.*, **60**, 1454 (1956). [g] V. P. Kolesov, A. M. Martynov, S. M. Shetlkhev, and S. M. Skuvatov, *Russ. J. Phys. Chem.*, **36**, 118 (1962). [h] J. P. McCullough, H. L. Finke, W. N. Hubbard, S. S. Todd, J. F. Messerly, D. R. Donslin, and G. Waddington, *J. Phys. Chem.*, **65**, 784 (1961). [i] D. W. Scott, D. R. Donslin, J. F. Messerly, S. S. Todd, I. A. Hossenlopp, T. C. Kinchloe, and J. P. McCullough, *J. Amer. Chem. Soc.*, **81**, 1015 (1959). [j] D. W. Scott, J. F. Messerly, S. S. Todd, I. A. Hossenlopp, D. R. Donslin, and J. P. McCullough, *J. Chem. Phys.*, **37**, 867 (1962). [k] ΔH_f calculated from Franklin's group equivalent method.[c] [l] N. Solimene and B. P. Dailey, *J. Chem. Phys.*, **22**, 2042 (1954). [m] J. L. Brandt and R. L. Livingston, *J. Amer. Chem. Soc.*, **76**, 2096 (1954). [n] V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963). [o] I. L. Karle and J. Karle, *ibid.*, **18**, 963 (1950). [p] L. Nygaard, I. Bojesen, T. Pederson, and J. Rastrup-Andersen, *J. Mol. Struct.*, **2**, 209 (1968). [q] H. Oosaka, *Bull. Chem. Soc. Jap.*, **15**, 31 (1940). [r] H. Oosaka, H. Sekine, and T. Saito, *ibid.*, **27**, 182 (1954). [s] W. F. Edgell, G. B. Miller, and J. W. Amy, *J. Amer. Chem. Soc.*, **79**, 2391 (1957). [t] "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966. [u] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Anderson, *Spectrochim. Acta*, **13**, 120 (1958). [v] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). [w] S. P. S. Porto, *J. Mol. Spectrosc.*, **3**, 248 (1958). [x] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952). [y] C. W. W. Hoffman and R. C. Livingston, *ibid.*, **21**, 565 (1953).

geometries for a number of fluorinated hydrocarbons. The first value for the heat of formation is that calculated for the experimentally determined geometry, the second for the geometry that minimizes the energy. The latter was calculated by a modification of a program written by Dr. A. Brown based on the SIMPLEX algorithm.[17]

MINDO/2 of course gives heats of atomization rather than heats of formation; these were converted to heats of formation using the heats of formation of gaseous atoms.

The overall agreement between the calculated and observed heats of formation is good, the average error being ±4 kcal/mol; indeed, the agreement may be even better than it appears to be at first sight since many of the experimental values are derived from electron impact appearance potentials rather than direct thermochemical measurements. The former are certainly less reliable and the older values in particular tend to be too large, leading to heats of formation that are too negative. It is perhaps significant that the two largest errors (9 kcal/mol) are for molecules ($CH_2{=}CH{-}CF_3$ and $CH_3CH_2CF_3$) whose heats of formation have been determined only from electron impact measurements and which are more negative than our calculated values. Note in particular that we correctly predict the order of stability of isomers, *e.g.*, $CH_3CF_3 > CH_2FCHF_2$, $CH_3CHFCH_3 > CH_3CH_2CH_2F$, and $m\text{-}C_6H_4F_2 > p\text{-}C_6H_4F_2 > o\text{-}C_6H_4F_2$. Note also that the heats of formation of highly fluorinated compounds (*e.g.*, CF_4, C_2F_6, hexafluorobenzene) are correctly predicted, implying that our procedure accounts well for steric effects in crowded molecules and for the increase in stability when two or more fluorine atoms are attached to the same carbon.

MINDO/2 fails to account for the dipole fields due to unshared pairs of electrons in hybrid AOs. This is an inevitable consequence of its neglect of one-center differential overlap. As a result, it overestimates the stability of compounds in which two such atoms are directly linked and correspondingly underestimates the length of the bond linking them. This failing is seen in the case of fluorine and difluorocarbene (Table IV). The error in the latter is very large since all three atoms have hybridized lone pairs. Table IV also lists two other molecules for which MINDO/2 gives poor re-

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(17) J. A. Nelder and R. Mead, *Comput. J.*, 7, 308 (1964).

Table IV. Heats of Formation and Bond Lengths in Some Additional Fluorides

	ΔH_f, kcal/mol at 25°C			
	Obsd	Calcd[a]	Error	Bond length, Å, calcd (obsd)
HF	−64.8[b]	−77.8	13.0	HF, 0.964 (0.917[c])
F_2	0[b]	−8.0	8.0	FF, 1.103 (1.418[d])
CF_2	−35.0[e]	−72.2	37.2	CF, 1.296; FCF, 107°
FC≡CF	−51.3 ± 15[b]	10.0	−61.3	CF, 1.293; CC, 1.195

[a] For calculated geometry. [b] See Table II, ref *d*. [c] G. A. Knipers, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **25**, 275 (1956). [d] Interatomic Distances, *Chem. Soc. Spec. Publ.*, No. **18** (1965). [e] See Table III, ref *c*.

Table V. Bond Angles in Ethylene and Its Fluoro Derivatives

Compound	$CH_2{=}CH_2$	$CH_2{=}CHF$	$CH_2{=}CF_2$		$CHF{=}CF_2$	$CF_2{=}CF_2$
Angle	CCH	CCF	FCF	HCH	FCF	FCF
Calcd	124.3°	123.3°	107.6°	119.3°	111.4°	111.8°
Obsd	122.2°[a]	120.9°[b]	109.2°	119.7°[c,d]	108.9°[e]	114.0°[f]

[a] L. S. Bartell and R. H. Bonham, *J. Chem. Phys.*, **31**, 400 (1959). [b] See Table III, ref *p*. [c] See Table III, ref *n*. [d] J. Carlos, C. H. Cheng, and S. H. Bauer, personal communication. [e] See Table III, ref *o*. [f] C. C. Costain and B. P. Stoieheft, *J. Chem. Phys.*, **30**, 777 (1959).

Table VI. Calculated Geometries of Substituted Ethylenes[a]

Molecule		Expt	Calcd	Ref
$(CF_3)_2C{=}CH_2$	R(C=C)	1.373	1.349	*b*
	R(C-C)	1.533	1.537	
	R(C-F)	1.327	1.333	
	R(C-H)	1.07	1.114	
	ϕ	10 ± 20°	0°	
$(CH_3)_2C{=}CH_2$	R(C=C)	1.331	1.336	*c*
	R(C-C)	1.505	1.501	
	R(C-H)		1.095	
	R(CH(CH₃))	1.113	1.104	
$CH_2{=}CHCH_3$	R(C=C)	1.336	1.339	*d*
	R(C-C)	1.501	1.486	
	R(C-H)	1.081	1.095	
	A(CCC)	124.3	124.9	
	A(HCH)	118.0	(120)	
	ϕ	0°	0.1°	
$CH_2{=}CHCF_3$	R(C=C)	1.282 ± 0.012	1.333	*e*
	R(C-C)	1.502 ± 0.008	1.520	
	R(C-H)	1.092 ± 0.014	1.090	
	R(C-F)	1.350 ± 0.002	1.341	
	A(CCC)	107.3 ± 1.7	124.9	
	A(HCH)	122.4	(120)	
	A(CCF)	112.5 ± 0.2	112.6	
	ϕ	21.7 ± 11.9°	0.5°	
$CF_2{=}CFCF_3$	R(C=C)	1.365 ± 0.027	1.360	*e*
	R(C-C)	1.506 ± 0.017	1.524	
	R(C-F)	1.323 ± 0.014	1.318	
	A(CCC)	110.0 ± 1.3	126.4	
	A(CC(CF₃)C)	123.4 ± 2.0	118.0	
	ϕ	40.3 ± 3.6°	6.2°	

[a] R(XY) = XY bond length (Å); A(XYZ) = XYZ bond angle (degrees); ϕ = angle of twist of C=C bond out of planarity. [b] R. L. Hilderbrandt, A. L. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, **74**, 1586 (1970). [c] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **32**, 824 (1960). [d] J. D. Swalen and C. A. Reilly, *ibid.*, **34**, 2122 (1961). [e] S. H. Bauer, presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971.

sults, hydrogen fluoride and difluoroacetylene. The error in the case of HF is not too surprising in view of the failure of this version of MINDO/2 to account correctly for the lengths of bonds to hydrogen. We have no explanation for the discrepancy in the case of difluoroacetylene though it must be admitted that the experimental value is more than usually uncertain.

B. Molecular Geometries. As Table III shows, MINDO/2 accounts reasonably well for the trends in bond lengths. It correctly predicts the contraction in CF bond length along the series $CH_3F > CH_2F_2 > CH_3F > CF_4$ and also the fact that CF bonds in vinyl fluorides are shorter than in corresponding saturated compounds.

The contraction in bond length along the series CH_3F, CH_2F_2, CHF_3, and CF_4 was accounted for some time ago by Walsh[18] in terms of changes in hybridization at the carbon center, an electronegative atom X tending to attract the CX bond electrons to it and consequently to increase the p character of the hybrid AO used by carbon to form the bond. This argument, which has apparently been rediscovered by Bent,[19] is supported by an analysis of our MINDO/2 wave functions. These results agree with the conclusions reached by Bernett[20] from an analysis of experimental bond angles.

(18) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947).
(19) H. A. Bent, *J. Chem. Phys.*, **33**, 1259 (1960).
(20) W. A. Bernett, *J. Org. Chem.*, **34**, 1772 (1969).

Table VII. Geometries of 1,3-Butadiene Derivatives

Molecule	R(C=C)	R(C-C)	R(C-F)	A(CCC)	ϕ	ΔH_f[a]	Ref
CF_2=CFCF=CF_2	1.360	1.467	1.320	127.2	46.6	−235.3	
	(1.336 ±0.018)	(1.488 ±0.018)	(1.323 ±0.006)	(125.8 ±0.6)	(47.4 ±2.4)		b
	1.360	1.461	1.321	130.3	13.8	−234.1	
	1.355	1.474	1.319	125.8	183.6	−236.5	
CF_2=CHCH=CF_2	1.346	1.449	1.316	121.6	180.9	−164.7	c, d
	1.356	1.473	1.314	124.8	41.5	−164.0	
	1.360	1.454	1.313	129.5	6.4	−162.5	
CF_2=CHCH=CH_2	1.350	1.464	1.315	127.9	4.2	−61.3	e
	1.352	1.464	1.309	124.1	181.8	−62.4	
			CH				
CH_2=CHCH=CH_2	1.333	1.474	1.096	125.7	43.8	33.2	
	1.335	1.472	1.094	123.8	181.9	32.4	
	(1.337)	(1.476)		(122.9)			f

[a] Heat of formation, kcal/mol at 25°. [b] C. H. Chang, A. L. Andreassen, and S. H. Bauer, *J. Org. Chem.*, **26**, 920 (1971). [c] R. M. Conrad and D. A. Dows, *Spectrochim. Acta*, **21**, 1039 (1965). [d] R. A. Beaudet, *J. Amer. Chem. Soc.*, **87**, 1390 (1965). [e] R. A. Beaudet, *J. Chem. Phys.*, **42**, 3758 (1965). [f] D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 173 (1962).

Table VIII. Bond Lengths and Bond Angles in Acetylene Derivatives

	R(C≡C)		R(C-C)		R(C-F)		R(C-H)		A(XCC)		
Molecule	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd	Ref
HC≡CH	1.207	1.201					1.059	1.050			a
HC≡CF	1.198	1.196			1.279	1.278		1.057			b
FC≡CF		1.195				1.293					
HC≡CCH_3	1.207	1.205	1.458	1.432			1.112	1.094	110.5	112.5	c
HC≡CCF_3	1.201	1.202	1.464	1.482	1.335	1.338		1.056	107.5	112.3	d
H_3CC≡CCH_3	1.213	1.203	1.467	1.431			1.116	1.102	110.7	113.2	e
F_3CC≡CCH_3	1.201	1.210	1.464	1.464	1.340	1.338	1.105	1.098			f
			C-CF_3								
			1.455	1.435							
			C-CH_3								
F_3CC≡CCF_3	1.199	1.196	1.472	1.486	1.333	1.332			110.8	111.4	g

[a] M. T. Christensen, D. R. Easton, B. A. Green, and H. W. Thompson, *Proc. Roy. Soc., Ser. A*, **238**, 15 (1956). [b] J. K. Tyler and J. Sheridan *Trans. Faraday Soc.*, **59**, 2661 (1963). [c] See Table III, ref *w*; L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955). [d] W. F. Sheehan and V. Schomaker, *J. Amer. Chem. Soc.*, **74**, 4468 (1952); *J. Chem. Phys.*, **19**, 1364 (1951). [e] M. Tanimoto, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.*, **42**, 2519 (1969). [f] V. W. Laurie, *J. Chem. Phys.*, **30**, 1101 (1959). [g] See Table VII, ref *b*.

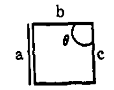
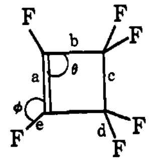
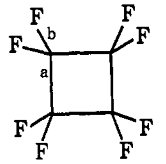
Note also that our calculations reproduce the increase in CC bond length on passing from ethane or 1,1,1-trifluoroethane to hexafluoroethane, the calculated bond length in the latter being very long (calcd 1.585 Å; obsd 1.56 Å). The CCF bond angles in CH_3CF_3 (calcd 111.9°; obsd 111.3°) and in C_2F_6 (calcd 111.3°; obsd 109.5°) are also in good agreement with experiment.

Our calculations also reproduce the observed bond angles in various ethylene derivatives (Table V). Note in particular the correct prediction that the FCF angle in olefins should tend to be tetrahedral whereas the HCH angle is trigonal.

Table VI compares calculated and observed geometries for a number of other fluorinated ethylene derivatives that have recently been studied, together with those of the parent hydrocarbons. The agreement between the calculated and observed bond lengths and bond angles is good. Note in particular the correct prediction that the C-C bond in a trifluoromethylethylene should be longer than that in a corresponding methylethylene. The only serious discrepancy occurs in the case of the last two compounds where unpublished electron diffraction studies indicate extensive twisting about the C=C bond. It is difficult to see any reason why this should be the case in 3,3,3-trifluoropropene (CH_2=CH-CF_3) and our calculations predict this molecule to be coplanar. In the case of hexafluoropropene (CF_2=CF-CF_3), a rather crowded molecule, our calculations do predict some twisting (6°) about the C=C bond but much less than that reported (40°). It must be admitted that the experimental values are very much at variance with chemical intuition and it should also be noted that MINDO/2 has given excellent estimates of the barriers to rotation about C=C bonds in other ethylene derivatives.[5]

Table VII shows calculations of equilibrium geometries and heats of formation for a number of butadiene derivatives. Our calculations agree with experiment in predicting the trans isomers of 1,1-difluoro- and 1,1,4,4-tetrafluoro-1,3-butadiene to be the most stable, as is the case for butadiene itself. The calculated bond lengths in butadiene, and in hexafluorobutadiene, also agree well with experiment. We also predict the gauche conformation of hexafluorobutadiene (CF_2=CF-CF=CF_2) to be more stable than the cis and the geometry calculated for the gauche isomer agrees with a recent structure determination by electron diffraction;

Table IX. Geometries of Compounds Containing Four-Membered Rings

Compound		Bond length, Å					Bond angle, deg		Dihedral angle, deg
		a	b	c	d	e	θ	ϕ	
	Calcd	1.343	1.484	1.552			94.0		
	Obsd[a]	1.342	1.517	1.566			94.2		
	Calcd	1.356	1.490	1.639	1.344	1.299	95.5	128.8	
	Obsd[b]	1.342	1.508	1.595	1.336	1.319	94.8	133.6	
	Calcd	1.569	1.346						10.0
	Obsd[b]	1.566	1.337						17.4

[a] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 369 (1969). [b] C. H. Chang, R. F. Porter, and S. H. Bauer, *ibid.*, **7**, 89 (1971).

however, even in this case we predict the trans isomer to be more stable although here the difference is too small to be unambiguously significant.

Table VIII compares calculated and observed geometries for a number of fluorinated acetylenes; data for the parent hydrocarbons are included. It will be seen that our results again agree quite well indeed with experiment; note in particular the very short CF bond length in fluoroacetylene and the correct prediction that the $C\equiv C$ bond length should be less in fluoroacetylene than in acetylene.

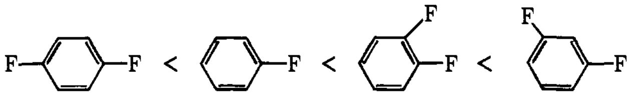
Table IX compares calculated and observed geometries for three compounds containing four-membered rings. The agreement is again very satisfactory. Note in particular the correct prediction that the CX_2–CX_2 bond in cyclobutene should be very long but that in hexafluorocyclobutene still longer; the latter is one of the longest CC bonds whose length has been measured. Note also that the CC bond in octafluorocyclobutane is also correctly predicted to be very long and also the correct prediction that C_4F_8 should be nonplanar.

Table X. First Ionization Potentials

Molecule	Expt[c]	Calcd[a]
Fluoromethane	12.85[b]	12.07
Fluoroethylene	10.37	10.33
1,1-Difluoroethylene	10.30	10.50
1,2-Difluoroethylene (cis)	10.25	10.11
1,2-Difluoroethylene (trans)	10.19	10.19
Trifluoroethylene	10.14	10.10
Tetrafluoroethylene	10.12	9.98
Fluorobenzene	9.21	9.62
1,2-Difluorobenzene	9.31	9.63
1,3-Difluorobenzene	9.33	9.78
1,4-Difluorobenzene	9.15	9.36
1,2,4-Trifluorobenzene	9.37	9.64
1,2,3,4-Tetrafluorobenzene	9.61	9.94
1,2,3,5-Tetrafluorobenzene	9.55	9.91
1,2,4,5-Tetrafluorobenzene	9.39	9.69
Pentafluorobenzene	9.84	10.04
Hexafluorobenzene	9.97	10.15

[a] Calculated from Koopman's theorem (*i.e.*, *minus* the Hartree-Fock energy of the highest occupied MO). [b] D. C. Frostand and C. A. McDowell, *Proc. Roy. Soc., Ser. A*, **241**, 194 (1957). [c] R. Bralsford, P. V. Harris, and W. C. Price, *ibid.*, **258**, 459 (1960).

C. Ionization Potentials. Table X compares calculated and observed first ionization potentials for a number of fluorinated hydrocarbons, the calculated values being given by Koopmans' theorem. It will be seen that the agreement is better than that given by other SCF MO procedures where the calculated orbital energies are commonly greater than the observed ionization potentials by 2–3 eV. Note the correct prediction of the trends in the series CH_4, CH_3F, CH_2F_2, CHF_3, CF_4 and C_2H_4, C_2H_3F, $C_2H_2F_2$, C_2HF_3, C_2F_4. Even more striking is the correct prediction of the trend in the series



and of the fact that on progressive fluorination the ionization potential of benzene first decreases and then rises again; this is in obvious contrast to the effect of progressive fluorination on the ionization potential of ethylene where the first fluorine *raises* the ionization

Table XI. Dipole Moments

Molecule	Dipole moment, D Expt	Dipole moment, D Calcd[a]
HF	1.92[g]	2.03
CH_3F	1.86[b]	2.11
CH_2F_2	1.96[c]	2.27
CHF_3	1.65[d]	1.80
$CH_2{=}CF_2$	1.37[e]	1.32
$F\text{-}C_6H_5$	1.66[f]	1.82
$m\text{-}F_2\text{-}C_6H_4$	1.62[g]	1.80

[a] Handbook of Chemistry and Physics, 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967–1968. [b] D. M. Larkin and W. Gordy, *J. Chem. Phys.*, **38**, 2329 (1963). [c] D. R. Lide, *J. Amer. Chem. Soc.*, **74**, 3548 (1952). [d] J. N. Shoslery and A. H. Sharbaugh, *Phys. Rev.*, **82**, 95 (1951). [e] A. Roberts and W. F. Edgell, *J. Chem. Phys.*, **17**, 742 (1959). [f] D. G. de Kowalski, P. Koheritz, and H. Selen, *ibid.*, **31**, 1438 (1959).

potential whereas further fluorination progressively reduces it.

It should be noted that calculations of ionization potentials, using a SCF MO π approximation, failed completely to reproduce these trends.[21]

D. Dipole Moments. Table XI compares calculated[22,23] and observed dipole moments of some fluorinated hydrocarbons. The agreement is obviously satisfactory. Note in particular the correct prediction of the rather strange changes in dipole moment along the series CHF_3, CH_2F_2, CHF_3 and the correct prediction of the moments of CH_2F_2 and $CH_2{=}CF_2$. While the absolute values for the moments are somewhat too large, so too are those given by recent *ab initio* SCF calculations.[24] The CNDO/2 method fails to reproduce the observed trends.[25]

[21] M. J. S. Dewar, A. J. Harget, and N. Trinajstić, unpublished results.

[22] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, 50, 1262 (1969),

[23] R. N. Dixon, *Mol. Phys.*, 12, 83 (1967).

[24] M. E. Schwartz, C. A. Coulson, and L. C. Allen, *J. Amer. Chem. Soc.*, 92, 447 (1970).

[25] J. A. Pople and M. S. Gordon, *ibid.*, 89, 4253 (1967).

Ground States of σ-Bonded Molecules. XVIII.[1] An Improved Version of MINDO/2 and Its Application to Carbonium Ions and Protonated Cyclopropanes[2]

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Abstract: (a) Modifications of MINDO/2 lead to correct CH bond lengths; (b) calculations are reported for several classical carbonium ions, the estimated heats of formation agreeing with experiment; (c) calculations for the various species derived by protonation of cyclopropane are in marked disagreement with *ab initio* calculations but in better accord with experiment; (d) calculations for protonated methylcyclopropanes support the π-complex theory of electrophilic addition to cyclopropane.

While the MINDO/2 method[5,6] has proved remarkably successful in a number of connections,[5–7] the original version[6] suffered from several serious defects. (1) Dipole moments were overestimated by 50%. (2) Bond lengths involving hydrogen were overestimated by 0.1 or 0.15 Å. (3) Strain energies of small rings were underestimated, the errors for cyclopropane and cyclobutene being 10 and 25 kcal/mol, respectively. (4) The treatment of heteroatoms was not satisfactory, the bond angles being much too large and large errors appearing in the lengths and bond energies of bonds involving pairs of adjacent heteroatoms.

One problem of much topical interest where reliable calculations would be of value is that concerning the existence and nature of "nonclassical carbonium ions." However, it seemed unlikely that calculations by MINDO/2 could prove useful in this connection until steps had been taken to remedy the first two objections above. Errors in calculated dipole moments imply errors in the calculations of charge distributions which could have serious consequences in the case of ions while errors in bond lengths would clearly be inconvenient in the comparison of related classical and nonclassical ions.

The first of these difficulties was overcome[1] by a change in the method used to determine the values of one-center integrals for spectroscopic data. Here we describe a further small modification which leads to correct CH bond lengths. The new parameters have been used in several calculations carried out recently in these laboratories.[7g] Here we have applied them to various carbonium ions and to the various species that can be formed by protonation of cyclopropane and its methyl and dimethyl derivatives.

Theoretical Procedure

The original version[6] of MINDO/2 led to dipole moments that were too large by *ca.* 50% and to CH bond lengths that were systematically too long by 0.1 Å. As noted above, the first of these defects has already been corrected[1] by a change in the estimation of one-center integrals.

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[1] Part XVII: M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5296 (1972).

[2] This work was supported by the Air Force Office of Scientific Research through Contract F44620-70-C-0121 and by the Robert A. Welch Foundation through Grant F-126. A preliminary account of some of it has appeared: N. Bodor and M. J. S. Dewar, *ibid.*, **93**, 6685 (1971).

[3] Robert A. Welch Postdoctoral Fellow.

[4] On leave of absence from the Chemical-Pharmaceutical Research Institute, Cluj, Romania.

[5] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

[6] N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

[7] (a) M. J. S. Dewar, E. Haselbach, and M. Shansal, *ibid.*, **92**, 3505 (1970); (b) N. Bodor and M. J. S. Dewar, *ibid.*, **92**, 4270 (1970); (c) A. Brown, M. J. S. Dewar, and W. W. Schoeller, *ibid.*, **92**, 5516 (1970); (d) M. J. S. Dewar and W. W. Schoeller, *ibid.*, **93**, 1481 (1971); (e) M. J. S. Dewar and J. S. Wasson, *ibid.*, **93**, 3081 (1971); (f) M. J. S. Dewar, M. Kohn, and N. Trinajstic, *ibid.*, **93**, 3437 (1971); (g) M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4290, 4291, 4292 (1971); (h) M. J. S. Dewar, Z. Náhlovská, and B. D. Náhlovský, *Chem. Commun.*, 1377 (1971).