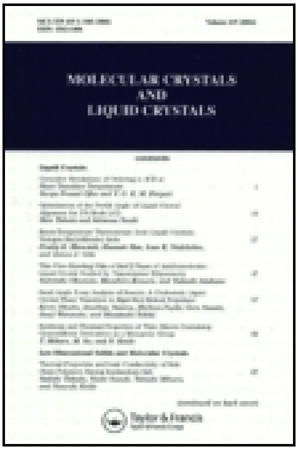

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CNDO/2-FPP POLARIZABILITIES*

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Polarization functions have been added to the CNDO/2 basis set to reproduce a minimal set of experimental polarizability tensors for 13 model molecules containing H, C, N, O, F, P, S, Cl, Se, and Br without affecting occupied molecular orbital energies or atom-in-molecule charges. The resulting CNDO/2-FPP program yields excellent molecular and atom-in-molecule polarizability tensors for almost any molecule containing these elements.

1. NEED FOR GOOD POLARIZABILITIES IN COHESIVE ENERGY CALCULATIONS

A valid objective is the theoretical understanding of the cohesive energy of organic ionic crystals and, in particular, of the partially ionic organic metals[1–4]. At present, the theoretical calculations must still follow the successful synthesis, but there is hope that one day they will mature to give predictive guidelines to synthetical research programs.

It has been shown that several lattice energies are important contributors to the overall cohesive energy U[1–5]:

$$U = E_M + E_{pol} + (E_d - E_r) + E_{cd} + E_\mu + E_t. \qquad (1)$$

E_M is the Madelung energy:

$$E_M = \sum_{i>j}\sum q_i\, q_j/r_{ij} \qquad (2)$$

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when the $\sum_i$, $\sum_j$ are lattice sums, the r_{ij} are interatomic distances in the crystal, and the q_i are atom-in-molecule partial charges. E_{pol} is the polarization energy:

$$E_{pol} = -(1/2) \sum_i \mathbf{F}_i^M \cdot \boldsymbol{\alpha}_i \cdot \mathbf{F}_i^M , \tag{3}$$

where the $\mathbf{F}_i^M$ are the Madelung electric fields, and the $\boldsymbol{\alpha}_i$ are atom-in-molecule polarizability tensors whose sum over the m atoms in a molecule equals the molecular polarizability $\boldsymbol{\alpha}_{mol}$[6,7]:

$$\boldsymbol{\alpha}_{mol} = \sum_{j=1}^{m} \boldsymbol{\alpha}_j . \tag{4}$$

E_{cd} is the charge-dipole energy:

$$E_{cd} = -\sum_i \mathbf{F}_i^M \cdot \boldsymbol{\mu}_i^{hyb} , \tag{5}$$

where the $\boldsymbol{\mu}_i^{hyb}$ are atom-in-molecule hybrid dipole moment components[6,7]. E_μ is the (small) dipolar energy:

$$E_\mu = \sum_i \sum_j (\boldsymbol{\mu}_i^{hyb} \cdot \boldsymbol{\mu}_j^{hyb}\, r_{ij}^{-3} - 3\boldsymbol{\mu}_i^{hyb} \cdot \mathbf{r}_{ij}\, \boldsymbol{\mu}_i^{hyb} \cdot \mathbf{r}_{ij}\, r_{ij}^{-5}). \tag{6}$$

E_t is the contribution due to metallic bands (small for TTF TCNQ[8]). E_d is the dispersion or van der Waals energy[4,5,9]:

$$E_d = - \sum_i \sum_j C_i\, C_j\, r_{ij}^{-6} \tag{7}$$

and E_r is an ad hoc Born-Mayer or Born-Landé repulsion energy[4,5,9].

In organic charge-transfer metals such as TTF TCNQ the Madelung, polarization, and dispersion energies are all of the same order of magnitude[4,5,10]; the charge-dipole energy is repulsive[4,5]. All these terms do not reproduce well the experimental cohesive energy or account for the partial charge transfer[4,5].

The atom-in-molecule polarizability tensors $\boldsymbol{\alpha}_i$ (and their scalar average $\bar{\alpha}_i$) are useful both for the polarization energy (Eq. (3)) and the dispersion energy (Eq. (7)) for either the London[11] (Eq. (8)) or Slater-Kirkwood[12] (Eq. (9)) forms for the coefficients C_i, C_j:

$$C_iC_j = \bar{\alpha}_i\,\bar{\alpha}_j(3/8)\sqrt{I_i}\,\sqrt{I_j} \tag{8}$$

$$C_iC_j = \bar{\alpha}_i\,\bar{\alpha}_j(3/2)(e\hbar/\sqrt{m_e})[(\bar{\alpha}_i/N_i)^{1/2} + (\bar{\alpha}_j/N_j)^{1/2}]^{-1} \tag{9}$$

where I_i is a typical electronic excitation energy (e.g. ionization energy) of the molecule to which atom i belongs, e is the electronic charge, m_e is the electronic mass, $\hbar$ is Planck's constant divided by 2π, and N_i is the "effective number of electrons" for atom i.

2. MINDO/3-FP POLARIZABILITIES IN REVIEW

Recent MINDO/3-FP (FP = finite perturbation) calculations of the atom-in-molecule polarizabilities $\underset{\sim}{\alpha}_i$ for small molecules[6] and for TTF, TTF$^+$, TCNQ, TCNQ$^-$, TMPD and TMPD$^+$ [7] have suffered from a lack of atomic polarization orbitals (PO) in the MINDO/3 basis set. This is evident in Table 1, which lists the principal values (α_1, α_2, α_3, and $\bar{\alpha} = (\alpha_1 + \alpha_2 + \alpha_3)/3$) of the molecular polarizability tensor $\underset{\sim}{\alpha}_{mol}$ for TTF°, TTF$^+$, TCNQ° and TCNQ$^-$ (α_1 is along the longest molecular axis, α_2 along the shorter in-plane axis, and α_3 is perpendicular to the molecular plane). The smallness of α_3 is particularly embarassing since it is the component in the direction of π-π overlap in these compounds, i.e. in the direction of charge transfer and high conductivity. The older semi-empirical molecular orbital programs CNDO/2 and INDO[13], when used to calculate molecular polarizabilities by the FP method, yield $\underset{\sim}{\alpha}$ values about twice smaller than those listed in Table 1[6,7].

Table 1 MINDO/3-FP Molecular Polarizabilities (Å^3) from Ref. 7

	TTF°	TTF$^+$	TCNQ°	TCNQ$^-$
α_1	25.74	41.16	72.79	169.77
α_2	17.62	20.05	21.71	24.66
α_3	4.96	4.90	4.48	4.56
$\bar{\alpha}$	16.10	22.04	32.99	66.33

3. DESIGN OF CNDO/2-FPP

The resolution of this deficiency is in adding expressly designed polarization orbitals (PO) to the minimum basis set valence orbitals (VO). This is easiest to do with CNDO/2, since INDO and MINDO/3 have more semiempirical parameters that must be adjusted for the added PO. The addition of PO to CNDO/2 is not new[14-18], but the way they are added is: the CNDO/2-finite perturbation method[6] is modified to create the CNDO/2-FPP (finite perturbation plus polarization) method, as follows:

(a) The energies of the occupied molecular orbitals are altered as little as it is possible.

(b) The atom-in-molecule partial charges q_i are modified as little as possible.

(c) The polarization orbitals are Slater-type atomic orbitals with parametrizable orbital exponents ζ_{PO}; they are 3 2p wavefunctions for H, 5 3d wavefunctions for C, N, O, F, P, S, and Cl, 5 4d's for Se and Br.

(d) The Mulliken resonance integrals β_A° are made adjustable for P, S, Cl, Se, and Br.

(e) The Wolfsberg-Helmholtz form of the off-diagonal core hamiltonian matrix elements $H_{\mu\nu}$ is multiplied by a parametrizable screening factor K (= 1 for VO); if two different K values arise because of the atoms μ and ν involved, their linear average is used.

(f) For the Se and Br VO, the parameters of Hase and Schweig[19] were used. For all PO the orbital electron affinities A_μ were set to zero, and the orbital ionization potentials were taken from experiment[20] (for Se, Br I_{PO} = -1.2, -1.6 eV were used).

(g) The parameters ζ_{PO}, K, β_A° were chosen so that the CNDO/2-FPP polarizabilities matched the experimental values for selected molecules as shown in Table 2.

Thus the CNDO/2-FPP method can extract remarkable fits to experimental $\underset{\sim}{\alpha}$ values while not affecting the other "good" features of unmodified CNDO/2, by reshuffling the unoccupied virtual orbitals, and by increasing somewhat the hybrid contributions μ_i^{hyb} to the molecular dipole moment. Care was taken that, if anything, a better fit to the experimental dipole moments was obtained than seen with unmodified CNDO/2.

Table 2 Choice of Parameters, and Fit for Model Molecules

Element	PO	ζ_{PO} (1/bohr)	$\beta_{\AA}$ (eV)	K	Model Mol.	Principal Values of Molecular Polarizability ($\AA^3$)			
						α_1	α_2	α_3	$\bar{\alpha}$
H	2p	0.620	--	0.25	H_2	1.07	0.69	0.69	0.81
					exp	1.03	0.71	0.71	0.82
C	3d	0.524	--	0.12	CH_4	2.55	2.55	2.55	2.55
					exp	2.60	2.60	2.60	2.60
N	3d	0.564	--	0.12	N_2	2.03	1.54	1.54	1.70
					exp	2.23	1.54	1.54	1.77
O	3d	0.580	--	0.12	H_2O	1.09	1.50	0.82	1.13
					exp	----	----	----	1.46
					CO_2	3.35	1.57	1.57	2.16
					exp	4.03	1.93	1.93	2.63
F	3d	0.754	--	0.12	HF	1.05	0.67	0.67	0.80
					exp	0.98	0.76	0.76	0.83
P	3d	0.680	-40	0.26	PH_3	4.19	4.15	4.15	4.16
					exp	----	----	----	4.27
S	3d	0.740	-42	0.26	H_2S	3.89	4.24	2.97	3.70
					exp	4.01	4.04	3.44	3.78
					CS_2	14.13	5.60	5.60	8.44
					exp	15.14	5.54	5.54	8.74
Cl	3d	0.977	-45	0.26	Cl_2	7.18	3.16	3.16	4.50
					exp	6.34	3.74	3.74	4.61
					HCl	3.09	2.03	2.03	2.39
					exp	2.81	2.50	2.50	2.60
Se	4d	0.920	-42	0.20	H_2Se	4.93	5.16	3.85	4.65
					exp	----	----	----	4.77
Br	4d	0.942	-45	0.20	HBr	4.24	2.96	2.96	3.38
					exp	4.22	3.31	3.31	3.61

4. APPLICATION OF CNDO/2-FPP

The CNDO/2-FPP method has been applied, to date, to 41 small and medium molecules, with excellent results, that prove the validity of the method. A very detailed report is in preparation[21]. We list in Table 3 results for a subset of 14 molecules; the polarizability anisotropy k is defined by:

$$k = \left[\frac{(\alpha_1 - \bar{\alpha})^2 + (\alpha_2 - \bar{\alpha})^2 + (\alpha_3 - \bar{\alpha})^2}{6\bar{\alpha}^2}\right]^{1/2} \qquad (10)$$

Table 3 Principal Values of α_1, α_2, α_3 of the Molecular Polarizability $\underset{\sim}{\alpha}_{mol}$ (Å^3), Polarizability Anisotropy k, and Molecular Dipole Moment μ (Debyes) for 14 Non-Model Molecules

Molecule	α_1	α_2	α_3	$\bar{\alpha}$	k	μ
C_2H_2	4.20	2.62	2.62	3.15	0.167	0
exp	4.73	2.87	2.87	3.49	0.178	0
C_2H_4	5.11	3.18	3.18	4.05	0.140	0
exp	----	----	----	4.22	0.143	0
C_2H_6	4.75	4.42	4.42	4.53	0.025	0
exp	4.98	4.21	4.21	4.47	0.057	0
C_6H_6	12.41	12.41	6.96	10.59	0.172	0
exp	12.27	12.27	6.65	10.40	0.180	0
CH_3COOH	5.80	5.50	4.43	5.24	0.080	1.674
exp	----	----	----	5.71	-----	1.75
C_2H_5OH	5.74	4.87	4.69	5.10	0.064	1.775
exp	5.76	4.98	4.50	5.08	0.072	1.73
NH_3	1.66	2.15	2.15	1.99	0.082	1.608
exp	2.41	2.12	2.12	2.22	0.044	1.47
CH_3CN	5.71	4.05	4.05	4.60	0.120	3.487
exp	5.74	3.85	3.85	4.48	0.141	3.92
CH_3NH_2	4.18	4.26	3.52	3.99	0.059	1.688
exp	----	----	----	4.01	0.054	1.326
CH_3Br	7.56	4.76	4.76	5.69	0.164	1.668
exp	6.91	4.96	4.96	5.61	0.116	1.79
Furan	8.08	9.40	4.85	7.44	0.181	0.327
exp	7.43	8.89	5.37	7.23	0.140	0.66
Pyrrole	9.87	9.49	5.42	8.26	0.173	2.285
exp	8.69	9.33	5.79	7.94	0.137	1.84
Thiophene	12.22	11.04	6.21	9.82	0.187	0.455
exp	10.15	10.14	6.70	9.00	0.128	0.60
SO_2	5.10	3.12	2.63	3.61	0.209	0.773
exp	----	----	----	3.89	0.175	1.61

The agreement in Table 3 between CNDO/2-FPP values and experimental data is truly remarkable. However, the N lone-pair polarizability in NH_3 is underestimated: this may implicate excited configurations and may be remedied in a FPP version of CNDO/S[22] that is in preparation.

The atom-in-molecule polarizabilities $\underset{\sim}{\alpha}_i$ obtained from CNDO/2-FPP for CH_3COOH, CH_3CN, CH_3NH_2 and C_6H_6 are shown in Figs. 1, 2, 3, and 4 respectively[23]. Finally, Table 4 lists the scalar-average atom-in-molecule polarizability $\bar{\alpha}_i$ for the atoms in 12 halomethanes.

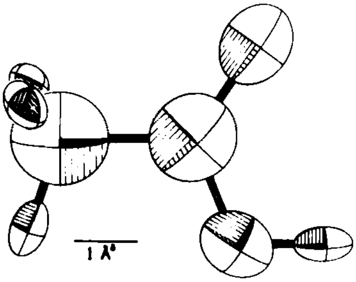

FIGURE 1 $\underset{\sim}{\alpha}_i$ for Acetic Acid

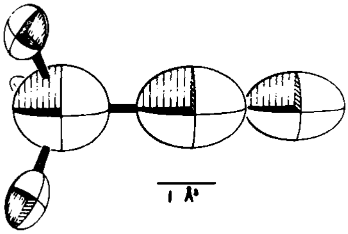

FIGURE 2 $\underset{\sim}{\alpha}_i$ for Acetonitrile

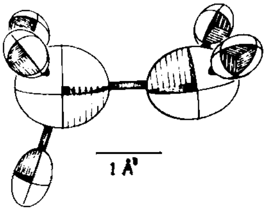

FIGURE 3 $\underset{\sim}{\alpha}_i$ for Methylamine

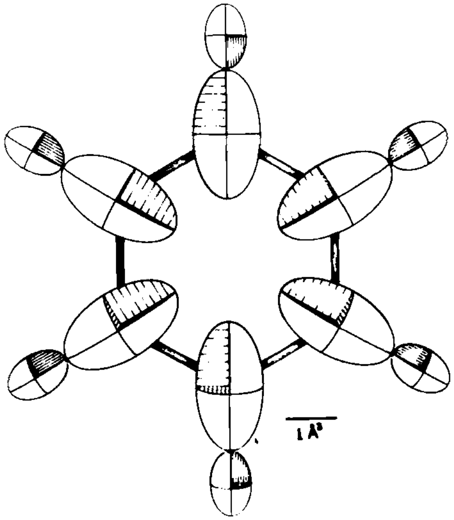

FIGURE 4 $\underset{\sim}{\alpha}_i$ for Benzene

Table 4 Scalar Averages $\bar{\alpha}_i$ (Å^3) of the Principal Axis Values of the Atom-in-Molecule Polarizability Tensor $\underset{\sim}{\alpha}_i$ for 12 Halomethanes CH_nX_m

Molecule	$\bar{\alpha}_C$	$\bar{\alpha}_H$	$\bar{\alpha}_X$
CH_3F	1.13	0.34	0.49
CH_2F_2	0.95	0.35	0.52
CHF_3	0.77	0.37	0.55
CF_4	0.65	---	0.57
CH_3Cl	1.25	0.33	2.20
CH_2Cl_2	1.32	0.32	2.32
$CHCl_3$	1.68	0.37	2.41
CCl_4	1.91	---	2.47
CH_3Br	1.32	0.34	3.35
CH_2Br_2	1.63	0.36	3.63
$CHBr_3$	2.39	0.40	3.79
CBr_4	3.19	---	3.89

The relative constancy of $\bar{\alpha}_H$ and $\bar{\alpha}_X$ within each subseries of four compounds, and the gradual changes in $\bar{\alpha}_C$ upon progressive halogenation all speak well of the power of CNDO/2-FPP as a predictor of molecular polarizability.

However, the demands of great convergence in the density matrix (better than 1 part in 10^8) and the onus of a large basis set require, alas, for a C_6H_6 run, 6 hours of DEC 1077 computer time. Runs on TTF and TCNQ await the installation of a faster IBM 4341 computer system at the University of Mississippi.

REFERENCES

1. R. M. Metzger, "Cohesive Energy Calculations and the Stabilization of Partially Ionic Lattices", elsewhere in this volume of *Mol. Cryst. Liquid Cryst.*
2. R. M. Metzger, *Ann. N.Y. Acad. Sci.* *313*, 145 (1978).
3. R. M. Metzger, "Cohesive Energy and Ionicity" in L. Alcácer, Ed., *The Physics and Chemistry of Low-Dimensional Solids* (NATO Advanced Study Institutes Series Vol. C56)(Reidel, Dodrecht, Holland 1980) page 233.

4. R. M. Metzger, "Cohesion and Ionicity in Organic Semi-Conductors and Metals" in R. M. Metzger, Ed., Crystal Cohesion and Conformational Energies (Topics in Current Physics, Vol. 26)(Springer, Berlin, Heidelberg, New York, 1981).
5. R. M. Metzger, J. Chem. Phys., **75**, 3087 (1981).
6. R. M. Metzger, J. Chem. Phys., **74**, 3444 (1981).
7. R. M. Metzger, J. Chem. Phys., **74**, 3458 (1981).
8. B. D. Silverman, Phys. Rev. **B16**, 5153 (1977).
9. D. E. Williams, "Transferable Empirical Nonbonded Potential Functions" in R. M. Metzger, Ed., Crystal Cohesion and Conformational Energies (Topics in Current Physics, Vol. 26)(Springer, Berlin, Heidelberg, New York, 1981).
10. H. A. J. Govers, Acta Cryst. **A34**, 960 (1978).
11. F. London, Z. phys. Chem. **B11**, 222 (1930).
12. J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).
13. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory (McGraw-Hill, New York, 1969).
14. D. W. Davies, Mol. Phys. **17**, 473 (1969).
15. J. J. C. Teixeira-Dias and J. N. Murrell, Mol. Phys. **19**, 329 (1970).
16. J. J. C. Teixeira-Dias and P. J. Sarre, J. Chem. Soc. Faraday Trans II **75**, 906 (1975).
17. H. Shinoda and T. Akutagawa, Bull. Chem. Soc. Japan **48**, 3431 (1975).
18. E. N. Svendsen and T. Stroyer-Hansen, Int. J. Quantum Chem. **13**, 235 (1978).
19. H. L. Hase and A. Schweig, Theoret. Chim. Acta (Berlin) **31**, 215 (1973).
20. C. E. Moore, Atomic Energy Levels Vol. I, National Bureau of Standards Circular 467 (National Bureau of Standards, Washington, D.C., 1949).
21. C. H. Rhee, R. M. Metzger, and F. M. Wiygul, "CNDO/2-FPP Atom-in-Molecule Polarizabilities", submitted to J. Chem. Phys.
22. J. Del Bene and H. H. Jaffé, J. Chem. Phys. **48**, 1807, 4050 (1968).
23. The drawings were executed with C. K. Johnson's program "OR TEP, A Fortran Ellipsoid Plot Program for Crystal Structure Illustration" ORNL-5138 (Oak Ridge National Laboratory, Oak Ridge, Tenn. 1972).