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special section

Quantitative prediction of molecular optical polarizability anisotropy: benzene, substituted benzene and rigid-rod oligomers

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Quantitative predictions of optical polarizability and its anisotropy are effected through a method that combines intrinsic molecular optical polarizability (as this is determined via semi-empirical quantum calculations) with inter- and intramolecular contributions to molecular optical polarizability (as those are manifested in depolarized Rayleigh scattering experiments). The approach is based on that proposed earlier by Dewar by which one can predict mean optical polarizabilities. Dewar's methodology is extended to predict not only the mean but also the anisotropy of the optical polarizability. It is shown that the technique is applicable to unsubstituted benzene and a number of substituted benzenes by quantitatively reproducing experimental values of mean optical polarizability and optical anisotropy simultaneously. The technique is further applied to model oligomers of three rigid-rod polymers, *cis*- and *trans*-poly(*p*-phenylene benzobisoxazole) as well as *trans*-poly(*p*-phenylene benzobisthiazole), to show excellent agreement with previously published experimental and theoretical results. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

It is common practice to employ semi-empirical quantum calculations to obtain an estimate of the components of the polarizability and hyperpolarizability tensors of isolated small organic molecules and oligomers. The need for reliable computation for these quantities has increased during recent years since more attention has turned to organic materials with fascinating, and sometimes useful, linear and non-linear optical properties. Most of the time computational predictions are used for qualitative comparisons only, the reason being the inability of the calculations to reproduce experimental results quantitatively.

In the case of polymers and oligomers, the importance of optical polarizability and its anisotropy may easily be shown by simply pointing out that a number of conformation-dependent properties of polymer chains depend on the anisotropic part of the (group or repeat-unit) polarizability tensor $\hat{\alpha}$. In particular, the optical configuration parameter $\Delta\alpha$, the mean-squared optical anisotropy $\langle\gamma^2\rangle$ and the molar Kerr constant ${}_{\mathrm{m}}K$ involve in their formulations the anisotropic part of the 'group' polarizability tensor[1].

Experimentally, $\Delta\alpha$ is obtained from strain birefringence measurements through the determination of the stress-optical coefficient C (ref. 2), while $\langle\gamma^2\rangle$ is obtained through depolarized Rayleigh scattering (DRS) measurements in dilute solutions[3]. The molar Kerr constant is obtained through electric birefringence experiments in dilute solutions[4]. Successful application of Flory's rotational isomeric state theory for the calculation of all these quantities requires reliable values of $\hat{\alpha}$ (ref. 1).

The valence-optical scheme (VOS) is the most frequently used method to determine $\hat{\alpha}$ for groups (repeat units and/or model compounds)[5]. It is well known, however, that VOS ignores inductive effects, and this causes a number of problems. A typical example is the strain birefringence of swollen networks[6]. The optical anisotropy of the swelling agent interferes with the measurement and sometimes the optical configuration parameter of the swollen sample may exceed that of the unswollen. The only proper way to solve the problem is to devise a methodology that accounts for these interactions. A reasonable starting point would be small molecules and model compounds of polymers.

This work is based on the observation that polarizabilities calculated by typical semi-empirical quantum programs refer to the isolated molecule. It is, however, well known that values of polarizabilities are strongly affected by the environment of the bond (or group) under consideration. The presented approach is based on the initial determination of the polarizability tensor components by a straightforward semi-empirical quantum approach. All results reported in this work are based on AM1 (Austin method 1)[7]. The components of the diagonalized polarizability tensor are then modified by applying a modified procedure suggested earlier by Dewar, who based his approach on work published earlier by Hush and Williams[8–10].

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Dewar has shown that application of his method, based on MNDO (medium neglect of differential overlap), produces mean polarizabilities of a large number of molecules with satisfactory accuracy. Previous work, however, did not address the important issue of optical anisotropy. Instead, it focused only on the determination of mean polarizability.

This paper contains the following sections. After a brief description of experimental considerations, the methodology is presented. This is followed by extensive comparisons of calculated optical polarizability values with experimental data taken from the literature and new experimental data generated for this purpose in this laboratory. After results on substituted benzene are presented, results on model compounds of rigid-rod polymers are shown.

EXPERIMENTAL CONSIDERATIONS

The squared optical anisotropy, which may be obtained through depolarized Rayleigh scattering experiments, is being defined in terms of $\hat{\alpha}$ through[11]:

$$\gamma^2 \equiv \tfrac{3}{2}\mathrm{Tr}(\hat{\alpha}\hat{\alpha}) \tag{1}$$

where Tr( ) denotes the trace of the matrix $\hat{\alpha}\hat{\alpha}$. In the case of polymers, one must consider the mean-squared optical anisotropy $\langle\gamma^2\rangle$.

Reliable comparison of predicted $\langle\gamma^2\rangle$ with experimental data is complicated when one considers that many times available experimental results for $\langle\gamma^2\rangle$ are inconsistent for the following reasons. What one measures in DRS is an 'effective' optical anisotropy $\langle\gamma^2\rangle_{\mathrm{eff}}$, which is essentially a function of intrinsic molecular optical anisotropy $\langle\gamma^2\rangle_{\mathrm{intrinsic}}$, the optical anisotropy due to the local field $\langle\gamma^2\rangle_{\mathrm{local\,field}}$, the optical anisotropy due to orientation correlation $\langle\gamma^2\rangle_{\mathrm{or\,corr}}$, the optical anisotropy induced by hard molecular collisions $\langle\gamma^2\rangle_{\mathrm{coll\,ind}}$ and the optical anisotropy due to pairs of density fluctuations $\langle\gamma^2\rangle_{\mathrm{pairs\,dens\,fluct}}$. Failure to account for *all* these terms plus the fact that many times the experimental results include unwanted Raman contributions are the main reasons for the scarcity of reliable experimental data.

Typical experimental values for optical polarizability anisotropy are obtained either in the gas phase or, especially for polymers, in solution with subsequent extrapolation to infinite dilution[12]. Most of the experimental values reported in this paper are from solutions. Each result is accompanied by a reference to facilitate locating experimental conditions and associated information. Experimental values for some of the compounds described below were generated in this laboratory. Detailed experimental measurements, conditions and data manipulation will be described in a forthcoming publication[13].

THEORY AND CALCULATIONS

A minimum-basis-set treatment is not expected to reproduce atomic (or molecular) polarizabilities. For example, values calculated from MNDO (medium neglect of differential overlap) and MINDO/3 (modified intermediate neglect of differential overlap) have been shown to be systematically low[8,14]. The error is naturally greatest in the case of components perpendicular to planar and linear molecules where the major contribution is due to atomic terms.

In this work semi-empirical calculations are employed to form the basis of a methodology that accounts for inductive effects (inter- and intramolecular contributions) to optical polarizability anisotropy $\langle\gamma^2\rangle$, and of course $\hat{\alpha}$. The proposed methodology is based on concepts found in previous work by Dewar and Stewart[8], Dewar, Yamaguchi and Suck[9] and Hush and Williams[10]. Those groups have developed a methodology based on a combination of MNDO and incorporation of the contribution of excitations from valence-shell orbitals to higher orbitals for free atoms.

In this interpretation the molecular polarizability anisotropies are determined by transitions within the valence shell, the contributions associated with transitions to the $n > 2$ levels being essentially isotropic. Following Hush and Williams one may write[10]:

$$\alpha_{\mathrm{mol}} = \alpha'_{\mathrm{mol}} + \sum_i \delta\alpha_{\mathrm{at}}(i) \tag{2}$$

with

$$\delta\alpha_{\mathrm{at}}(i) = \alpha_{\mathrm{at}}(i) - \alpha_{\mathrm{at,c}}(i) \tag{3}$$

where the sum is carried over all atoms i of the molecule. Here, focus is on calculating *simultaneously* $\bar{\alpha}$ and $\hat{\alpha}$ (and subsequently $\langle\gamma^2\rangle$) instead of just simply $\bar{\alpha}$. The symbols in equation (2) are as follows: α_{mol} is the apparent molecular polarizability component; α'_{mol} is the molecular polarizability component that results from the semi-empirical calculations; and $\sum_i \delta\alpha_{\mathrm{at}}(i)$ is the polarizability component modification applied to all the atoms in the molecule. In equation (3): $\delta\alpha_{\mathrm{at}}(i)$ is the difference between the experimental polarizability for atom i, $\alpha_{\mathrm{at,c}}(i)$, and the polarizability that one obtains from the semi-empirical procedure. Equation (3) outlines the procedure for obtaining individual atomic contributions. Hush and Williams employ $\delta\alpha_{\mathrm{at}}(i)$ values of $0.576 \times 10^{-24}\,\mathrm{cm}^3$ for Li to F and $0.334 \times 10^{-24}\,\mathrm{cm}^3$ for H. They point out that absolute values of both molecular and free-atom polarizabilities are usually underestimated by any semi-empirical method.

This work follows Hush and Williams by obtaining the quantity $\alpha_{\mathrm{mol}} - \sum_i \delta\alpha_{\mathrm{at}}(i)$ (i.e. polarizability minus sum of polarizabilities of constituent free atoms) for several molecules (benzene, chlorobenzene and bromobenzene). Observed and calculated values are in reasonable agreement, thus suggesting that it is appropriate to modify the predicted molecular polarizabilities for the discrepancy in atomic polarizabilities obtained by the same method.

Dewar extended further the concept developed by Hush and Williams by suggesting that the atomic contribution for a given atom should be less in directions where it forms bonds than in a direction orthogonal to them. In addition, the contribution should be less along more polarizable bonds than along less polarizable ones. To support these assertions, Dewar points out that MNDO gives very satisfactory results for linear multi-bonded molecules along the molecular axis such as N_2, CO, CO_2, N_2O, C_2H_2 and C_2N_2.

This work relies on the semi-empirical method AM1, a third-generation procedure devised by Dewar[15,16]. The

Table 1 Original and modified Dewar atomic contributions and corresponding polarizability tensor components

Atom	Modified Dewar values (Å^3)	Original Dewar values (Å^3)	Tensor component affected
H	+0.25	+0.25	α_{xx}, α_{yy}, α_{zz}
C	+0.85	+0.60[a]	α_{zz}
Cl	+0.75 +1.5	+1.0 +2.0[b]	α_{xx}, α_{yy} α_{zz}
Br	+1.5 +2.5	N/A N/A	α_{xx}, α_{yy} α_{zz}

[a] 0 along multiple bonds, +0.1 in plane for aromatic rings and +0.3 for all other situations

[b] +1.5 is suggested for intermediate orientations

Table 2 Comparison of calculated to experimental optical anisotropies (Å^6) of methyl-substituted benzenes

Compound	AM1	Dewar	Modified Dewar	Flory[11]	LeFevre[14]	Exp. data, this lab.
Benzene	78.0	34.0	13.9	13.2	14.5	14.1 ± 0.1
Toluene	84.0	38.4	17.1	18.4	18.0	20.0 ± 0.1
Cumene	86.9	41.3	20.1	20.8	N/A	22.0 ± 0.1
t-Butylbenzene	91.3	44.9	23.2	20.6	N/A	20.1 ± 0.1
o-Xylene	90.0	42.4	19.8	N/A	24.0	23.0 ± 0.1
m-Xylene	89.8	42.3	19.7	N/A	28.0	24.1 ± 0.1
p-Xylene	95.2	47.3	24.4	N/A	22.0	25.9 ± 0.1
1,3,5-Trimethylbenzene	94.4	45.0	21.3	N/A	20.0	26.8 ± 0.1
Hexamethylbenzene	119	62.6	33.8	N/A	34.0	42.2 ± 0.2

values for the components of the polarizability tensor that come from AM1 represent those of a geometry-optimized, isolated molecule. AM1, like MNDO, calculates electrostatic polarizabilities for the isolated molecule *in vacuo*. Furthermore, new atomic contributions are proposed based on equation (3). The final step combines those contributions with the AM1 results (see the following section on how to apply the method) to reproduce experimental mean and anisotropy optical polarizability data.

Table 1 shows values of atomic contributions for H, C, Cl and Br developed based on the methodology described above. Comparison is made with the original Dewar values that have shown good agreement with experimental values of mean optical polarizability[8].

RESULTS AND DISCUSSION

Because of its symmetry, benzene has equal in-plane components of polarizability: $\alpha_{xx} = \alpha_{yy}$. The experimental mean optical polarizability and the optical polarizability anisotropy of benzene are[11]:

$$\bar{\alpha} = 10.4\,\text{Å}^3 \tag{4}$$

and

$$\gamma^2 = 13.8\,\text{Å}^6 \tag{5}$$

The AM1 values for the diagonalized polarizability tensor are:

$$\alpha_{xx} = \alpha_{yy} = 10.17\,\text{Å}^3 \tag{6}$$

$$\alpha_{zz} = 1.34\,\text{Å}^3 \tag{7}$$

Employing equations (6) and (7) one obtains for the mean polarizability:

$$\bar{\alpha} = \tfrac{1}{3}\mathrm{Tr}(\boldsymbol{\alpha}) = 7.23\,\text{Å}^3 \tag{8}$$

and

$$\gamma^2 = \tfrac{3}{2}\mathrm{Tr}(\hat{\boldsymbol{\alpha}}\hat{\boldsymbol{\alpha}}) = 78.0\,\text{Å}^6 \tag{9}$$

where:

$$\hat{\boldsymbol{\alpha}} = \boldsymbol{\alpha} - \bar{\alpha}\mathbf{E}_3 \tag{10}$$

with $\mathbf{E}_3$ being the identity matrix of order 3. Applying Dewar's methodology one obtains for the H and C atoms in benzene:

for H

$$\alpha_{xx,\mathrm{c,H}} = \alpha_{xx} + 6 \times 0.25 \tag{11}$$

$$\alpha_{yy,\mathrm{c,H}} = \alpha_{yy} + 6 \times 0.25 \tag{12}$$

$$\alpha_{zz,\mathrm{c,H}} = \alpha_{zz} + 6 \times 0.25 \tag{13}$$

for C

$$\alpha_{zz,\mathrm{c,H}} = \alpha_{zz} + 6 \times 0.85 \tag{14}$$

The new tensor components for benzene are now:

$$\alpha_{xx,\mathrm{c}} = \alpha_{xx,\mathrm{c,H}} = 11.67\,\text{Å}^3 \tag{15}$$

$$\alpha_{yy,\mathrm{c}} = \alpha_{yy,\mathrm{c,H}} = 11.67\,\text{Å}^3 \tag{16}$$

$$\alpha_{zz,\mathrm{c}} = \alpha_{zz,\mathrm{c,H}} + \alpha_{zz,\mathrm{c,C}} = 7.94\,\text{Å}^3 \tag{17}$$

The new value for the mean polarizability now becomes $\bar{\alpha} = 10.43\,\text{Å}^3$ and for the anisotropy $\gamma^2 = 13.91\,\text{Å}^6$. Agreement with the experimental values of 10.4 Å^3 and 13.9 Å^6, respectively, is perfect within experimental error.

Table 2 shows comparisons for optical anisotropies (Å^6) for a number of methyl-substituted benzenes. The column under the heading 'AM1' shows the results from AM1 calculations from energy-minimized structures[16]. The column labelled 'Dewar' gives the results that one obtains applying the original Dewar method. The column labelled 'Modified Dewar' presents the results one obtains after applying the modified Dewar method. The next column presents results from Flory's experimental work from depolarized Rayleigh scattering experiments[11]. LeFevre's experimental results[14] (from

Table 3 Comparison of calculated to experimental mean optical polarizabilities (Å^3) of methyl-substituted benzenes

Compound	AM1	Dewar	Modified Dewar	Experiment	Ref.
Benzene	7.23	10.33	10.43	10.42	17
Toluene	8.65	12.55	12.35	12.31	17
Cumene	11.09	16.59	15.79	15.99	This lab.
t-Butylbenzene	12.17	18.47	17.37	17.86	This lab.
o-Xylene	10.02	14.72	14.22	14.18	18
m-Xylene	10.08	14.78	14.28	14.23	17
p-Xylene	10.14	14.84	14.34	14.28	18
1,3,5-Trimethylbenzene	11.50	17.00	16.20	16.14	17
Hexamethylbenzene	15.67	23.57	21.87	20.81	19

Table 4 Comparison of calculated to experimental optical anisotropies (Å^6) of halogen-substituted benzenes

Compound	AM1	Dewar	Modified Dewar	Flory[11]	LeFevre[14]
Chlorobenzene	115.5	48.4	28.2	29	33
Bromobenzene	133.6	N/A	37.6	37	41
p-Chlorotoluene	132.9	62.5	40.8	39.5	N/A
p-Bromotoluene	154.8	N/A	53.5	51.9	N/A

Table 5 Comparison of calculated to experimental mean optical polarizabilities (Å^3) of halogen-substituted benzenes

Compound	AM1	Dewar	Modified Dewar	Experiment	Ref.
Chlorobenzene	8.28	12.5	12.23	12.25	17
Bromobenzene	8.70	N/A	13.48	13.62	17
p-Chlorotoluene	9.80	14.8	14.25	13.7	20
p-Bromotoluene	10.22	N/A	15.5	14.8	20

Kerr-effect measurements) are presented in the following column. The last column shows experimental data from this laboratory. The agreement is excellent, within experimental error, for all molecules in this table.

It is, of course, necessary that the new method reproduces not only values of anisotropy but also values of the mean optical polarizability produced earlier by Dewar. *Table 3* presents results for the mean optical polarizability for the same compounds as in *Table 2*.

Tables 4 and *5* report results for several halogen-substituted benzenes, mainly chloro- and bromo-substituted, for which experimental results currently exist. *Table 4* contains values of polarizability anisotropy while *Table 5* contains values for mean polarizabilities.

As shown in *Tables 2* and *4*, excellent agreement with experiment is obtained for optical anisotropy values when calculated by the modified Dewar method. This holds true for the methyl-substituted benzenes and the halogen-substituted benzenes. Incorporation of inter- and intramolecular contributions to molecular optical polarizability through equations (2) and (3) following Hush and Williams' procedure gives more realistic molecular polarizability components. To highlight the extent of agreement between the optical anisotropy predicted by the modified Dewar method and the experimental optical anisotropy determined by depolarized Rayleigh scattering photometry, let us consider the values for benzene as shown in *Table 2*. The experimental optical anisotropy for benzene is 14.1 Å^6. The calculated optical anisotropy of benzene using the AM1 method is about 450% higher than the experimental value. Using the original Dewar method, an optical anisotropy of approximately 140% higher than the experimental value is obtained for benzene. The calculated optical anisotropy by the modified Dewar method is about 1% lower than that obtained experimentally. Overall, this method produces optical anisotropy values for the benzene compounds that are within 20% of the experimental values. While AM1 calculates electrostatic polarizabilities for isolated molecules *in vacuo*, the modified Dewar method accounts for the inductive effects on molecular polarizability. The most substantial change is in the α_{zz} component, resulting in a more isotropic polarizability ellipsoid.

Tables 3 and *5* show excellent agreement between the mean optical polarizabilities calculated by the modified Dewar method and experimentally determined values for all the compounds studied here. The experimental mean optical polarizability of benzene is 10.42 Å^3. For the purpose of comparison, in the case of benzene, AM1 predicts a value that is about 30% less than the experimental value. The value calculated by the original Dewar method is about 1% lower than the experimental value obtained by Denbigh[17]. Using the modified Dewar method, a mean optical polarizability of 0.1% higher than the experimental value is obtained. Again, it should be noted that such a level of agreement is observed for all methyl-substituted benzenes and halogen-substituted benzenes when applying the modified Dewar method. Hence, the modified Dewar method accurately predicts both the mean and the anisotropy of the optical polarizability.

RIGID-ROD OLIGOMERS

The main motivation behind this effort is to predict optical properties of polymer chains. As a first step it was decided to study oligomers. Model compounds of three rigid-rod chain molecules were chosen for application of the method. These are poly(*p*-phenylene benzobisoxazole) (*cis* and *trans*) and poly(*p*-phenylene benzobisthiazole) (*trans* only). The structure of the model oligomer of *cis*-poly(benzobisoxazole) used for the calculations is shown in *Figure 1*.

Literature values, both experimental and from earlier calculations based on atomic additivity and/or VOS, were taken from a paper by Mark *et al.*[21]. Collective

Table 6 Comparison of average polarizabilities and anisotropic ratios for model rigid-rod compounds

Polymer	$\bar{\alpha}$			δ		
	AA[22]	VOS[17]	This work	Mark[21]	This work	Berry[23]
cis-PBO	25.0	26.9	41.86	0.30	0.40	N/A
trans-PBO	25.0	26.9	43.22	0.30	0.43	N/A
trans-PBT	30.0	34.2	49.83	0.23	0.40	0.50

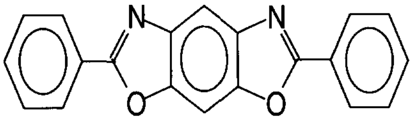

Figure 1 Model oligomer of *cis*-poly(benzobisoxazole) (*cis*-PBO)

results are presented in *Table 6*. The second column of this table presents results from the atomic additivity (AA) method[22]. This is followed by results from the valence optical scheme[17]. Results in these two columns should be compared with the results given in the fourth column, which contains predictions of the modified Dewar methodology. Anisotropic ratios for all three polymers are given in the next three columns. For reasons of straightforward comparison, the definition of the anisotropic ratio, as this is used by Mark *et al.*, is employed[21]:

$$\delta^2 = \frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2} \quad (18)$$

The AA method does not allow the calculation of individual components of the polarizability tensor, and therefore no information is provided for δ from this method. The last column contains only one number, which comes from light-scattering measurements on solutions of *trans*-PBT in methanesulfonic acid by Berry *et al.*[23]. They have shown that in the cylindrical approximation the anisotropic ratio should be equal to 0.5. Prediction based on the modified Dewar methodology is equal to 0.40, a marked improvement over the value of 0.23 resulting from the VOS method. Closer inspection of the predictions of the three methods shown in this table confirms that both VOS and atomic additivity underestimate mean polarizabilities. This, however, should not come as a surprise since neither of those methods has a mechanism to incorporate contributions from the isolated molecule's environment.

CONCLUDING REMARKS

It seems worth while to compare the outlined methodology to the important work of Applequist. It is felt that the presented findings are in agreement with the comments of Applequist that result from the application of atom dipole interactions for molecular optical properties[24]. Applequist has also, more recently, published results on the application of the Olson–Sunberg model to aliphatic and aromatic hydrocarbons[25]. While both this work and Applequist's are aiming to provide a rational means of treating polarizability phenomena and increase understanding of the same, the methodologies differ from each other. The method presented here is based on quantum-mechanical calculations as opposed to the atom monopole–dipole interaction model employed by Applequist.

Applequist acknowledges that part of the motivation of his study came from findings from quantum-mechanical calculations showing that the dipole polarizability parallel to the bond axis has a charge-transfer contribution ranging from 15 to 90% of the total axial polarizability[25]. Therefore, results presented in this paper should be complementary to the application of the Olson–Sunberg model as it was employed by Applequist.

Close inspection of the effect that the modified Dewar method has on the isolated polarizability components suggests a number of interesting points. First, it reveals that the most dramatic effect is on the α_{zz} component, thus producing a more isotropic polarizability ellipsoid. This is in agreement with Dewar's expectations. Secondly, it confirms that intra- and intermolecular correlation strongly affects polarizability components and that one definitely needs to account for this phenomenon not only for calculations but also experimentally[26].

The choice of AM1 semi-empirical Hamiltonian was dictated by the fact that Dewar had relied on MNDO whose parameters are similar to AM1. Another consideration behind using AM1 is the speed of calculations involved as compared to *ab initio* methods. Selection of a better set of parameters would not change the methodology but only affect the magnitude of the corrections.

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REFERENCES

1 Flory, P. J. *Macromolecules* 1974, **7**, 381
2 Galiatsatos, V. *Trends Polym. Sci.* 1993, **1**, 20
3 Sen, S., Galiatsatos, V. and Patterson, G. D. *J. Chem. Phys.* 1995, **103**, 892
4 Riande, E. and Saiz, E. 'Dipole Moments and Birefringence of Polymers', Prentice Hall, Englewood Cliffs, NJ, 1992
5 Galiatsatos, V. *J. Inorg. Organometal. Polym.* 1991, **1**, 449
6 Galiatsatos, V. and Mark, J. E. *Polym. Bull.* 1987, **17**, 197
7 Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. and Stewart, J. J. P. *J. Am. Chem. Soc.* 1985, **107**, 3902
8 Dewar, M. J. S. and Stewart, J. J. P. *Chem. Phys. Lett.* 1984, **111**, 416
9 Dewar, M. J. S., Yamaguchi, Y. and Suck, S. H. *Chem. Phys. Lett.* 1978, **59**, 541

10 Hush, N. S. and Williams, M. L. *Chem. Phys. Lett.* 1970, **6**, 163

11 Suter, U. W. and Flory, P. J. *J. Chem. Soc., Faraday Trans. (II)* 1977, **73**, 1521

12 Bridge, N. J. and Buckingham, A. D. *Proc. R. Soc. (A)* 1966, **295**, 334

13 Sen, S. and Galiatsatos, V. manuscript in preparation

14 LeFevre, C. G. and LeFevre, R. J. W. *Rev. Pure Appl. Chem.* 1955, **5**, 261

15 Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.* 1977, **99**, 4899

16 Biosym Technologies Inc. MOPAC 6.0

17 Denbigh, K. G. *Trans. Faraday Soc.* 1940, **36**, 936

18 Batsanov, S. S. 'Refractometry and Chemical Structure', Consultants Bureau, New York, 1961

19 Sanyal, N. K., Ahmed, P. and Dixit, L. *J. Phys. Chem.* 1973, **77**, 2552

20 Landolt-Börnstein 'Zahlenwerte und Functionen', Vol. 1 (3), Springer-Verlag, Berlin, 1951

21 Bhaumik, D., Jaffe, H. H. and Mark, J. E. *Macromolecules* 1981, **14**, 1125

22 Miller, K. J. and Savchick, J. A. *J. Am. Chem. Soc.* 1979, **101**, 7206

23 Berry, G. C., Wong, C. P., Venkatraman, S. and Chu, S. G., Air Force Tech. Rep. AFML-TR-79-4115, 1979

24 Applequist, J. *Acc. Chem. Res.* 1977, **10**, 79

25 Applequist, J. *J. Phys. Chem.* 1993, **97**, 6016

26 Sen, S. and Galiatsatos, V. *Rev. Sci. Instrum.* 1994, **65**, 3511