The polarizability and second hyperpolarizability of some azabenzenes

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The average polarizability and second hyperpolarizability of some azabenzenes are reported and interpreted. A rule allowing the development of basis sets for complex molecules from those of appropriately defined fragments or models of them has been proposed and successfully tested.

The azabenzenes are compounds of considerable interest,[1-4] and an important variation of aromatic (or potentially aromatic) molecules,[1] which are instrumental in the understanding of electric nonlinearities[5,6] (Fig. 1).

Thus, we (a) report the electric property values of the azabenzenes and interpret these results employing simple concepts; and (b) provide evidence for a hypothesis according to which it is possible to develop basis sets for complex molecules employing the functions suitable for describing the electric polarizability α and hyperpolarizability γ of appropriately defined molecular fragments or models of them.

For the computations we have employed the CHF-PT-EB-CNDO method.[7-9] The basis sets are defined as follows with convergence criteria given in Ref. 10: (a) The ring orbitals have been optimized with respect to α and γ of benzene and are given in Ref. 9; and (b) the nitrogen orbitals have been optimized with respect to α and γ of N_2 (Table I) and are N: $2s(1.95)$, $2p(1.95)$, $3s(0.5582)$, $3p(0.5)$.

It is noted that the choice of the right basis set is essential for the correct determination of α and γ by any theoretical method. Our general approach to this important problem has been comprehensively analyzed in the preceeding article and in Ref. 8.

In the three molecules, for which there are available experimental results (pyridine, pyridazine, and pyrazine) we observe (Table II) that our method gives results of comparable quality to the elaborate computational procedure of Mulder *et al.*[11] and of better quality than the values given by CNDO/S-CI.[12] This indicates that the nitrogen basis is balanced.

This observation supports the stated conjecture and indicates that the properties of the whole molecule may

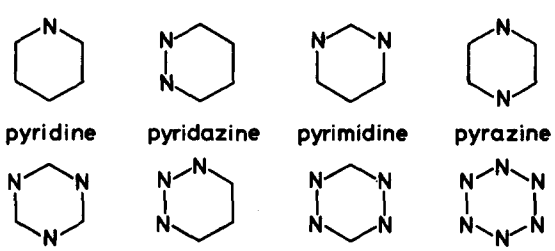

FIG. 1. Structure of the azabenzenes that were considered.

TABLE I. The polarizability, second hyperpolarizability of H, C, N, and N_2 in a.u. The electronegativities of the elements are also reported.

Species	α	γ	Electronegativity
H	4.5[b]	1332[e]	2.2[g]
C	12.0[c]	2350[c]	2.5[g]
N	7.6[c]	630[c]	3.0[g]
N_2[a]	11.8[d]	1440 ± 160[f]	

[a] It is noted that with the optimized orbitals (see the text) we find $\alpha = 8.7$ a.u. and $\gamma = 1440$ a.u.
[b] Reference 22.
[c] Reference 23.
[d] Reference 24.
[e] Reference 14.
[f] Reference 25.
[g] Reference 26.

be considered as functions of the properties of its parts.[13] If this hypothesis is judiciously applied, it will facilitate the computation of polarizabilities and second hyperpolarizabilities of large and complex molecules for which experimental property values are not cited in the literature.

We note that substitution of a CH group by a nitrogen has a much more pronounced effect on the rate of change of γ than α. For example, employing as a reference point the mean value of α, the difference between the maximum and minimum values is 18%, while the corresponding value for γ is 53%. This observation, which underlines the difference in sensitivity between the polarizability and the second hyperpolarizability in reflecting changes of the molecular structure, can be understood by invoking perturbation theory arguments according to which γ is proportional to the inverse of the third power of state energy differences while α is inversely proportional to the first.[14]

The substitution of CH groups by nitrogen leads, in general (there is only one exception—that is 1,2,3 triazine—where we have a marginal increase in γ in comparison to that of benzene), to a decrease in both α and γ.

This result can be rationalized by considering, that nitrogen has lower γ than both C and H while the polarizability of N is lower (less than half) than the sum of polarizabilities of C and H (Table I). An alternative expression of this rationalization is that N has higher electronegativity than both C and H (Table I). The exceptional value for the second hyperpolarizability of 1,2,3-triazine may be due to the concentration of electro-

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TABLE II. The polarizability and second hyperpolarizability of some azabenzenes[a,b] in a.u. (conversion factors to esu and SI are given in Refs. 7–9).

		α				γ	
No.	Molecule[c]	CNDO/S-CI[d]	*Ab initio*[e]	Present work	Experiment[f]	Hückel SCF[g]	Present work
1.	Pyridine	61.4 (4.2%)[h]	63.0 (1.7%)[h]	65.6 (2.3%)[h]	64.1	834	19 700
2.	Pyridazine	62.6 (5.6%)[h]	59.6 (0.5%)[h]	60.6 (2.1%)[h]	59.3	834	19 400
3.	Pyrimidine	57.6	57.9	61.6			16 700
4.	Pyrazine	59.7 (1.5%)[h]	59.4 (2%)[h]	60.5 (0.2%)[h]	60.6	834	15 800
5.	*s*-triazine		53.3	62.1			13 800
6.	1,2,3-triazine			66.0			26 300
7.	*s*-tetrazine		53.1	60.1			18 700
8.	Hexazine			54.7			10 400

[a] For comparison we note that the experimental values for the polarizability and the second hyperpolarizability of C_6H_6 are 69.5 a.u. (Ref. 16) and 24 500 a.u. (Ref. 17).

[b] The azabenzenes not reported failed to converge in the EB-CNDO SCF procedure.

[c] The geometries are defined in: 1: Ref. 18, 2: Ref 19, 3: Ref. 20, 4: Ref. 21, 5: Ref. 21, 8: Ref. 15, 6: The bond lengths and angles for 1,2,3-triazine are mean values, determined from the relevant azabenzene structures defined above. The coordinates are available on request. 7: The employed N–C bond length has been averaged, from those quoted in Ref. 21, while the employed angles and the N–N distance are also from Ref. 21.

[d] Only singly excited configurations have been employed. (Maximum of 60 configurations used.) (Reference 12.)

[e] An *ab initio* LCAO-MO-SCF wave function, where the possible incompleteness of the AO basis set has been corrected by employing a nonempirical, Unsöld procedure, was used (Ref. 11).

[f] These results are from Ref. 11.

[g] These values are taken from Ref. 6.

[h] The numbers in the parenthesis denote the percentage by which the theoretical results differ from the experimental.

negative centers on one side of the molecule and electropositive on the other which leads to a concentration of charge on the former and thus to higher properties.

It is worth noting that the second hyperpolarizability, being a very sensitive property, reflects the transfer to azabenzenes, of an interesting feature of N_2, i.e., molecular nitrogen has larger properties than two noninteracting atoms of N (Table I). Thus we observe (Table II)

(a) γ(pyridazine) > γ(pyrimidine) > γ(pyrazine),
(b) γ(triazine) > γ(*s*-tetrazine) > γ(*s*-triazine).

Hexazine[1,15] is an interesting case where one may see, quantitatively, the effect of bonding, on the magnitude of the second hyperpolarizability of a multiatom molecule. Thus we note that the part of γ which is due to the interaction of the nitrogen atoms is (approx) equal to 6560 ($=10\,400 - 6 \times 640$) a.u., i.e. about twice that associated with noninteracting atoms. Further, it is observed that only 1/7 (approx) of the property which is due to the various interactions is associated with the interaction of neighboring atoms (Tables I and II).

Finally, we note that the computed polarizabilities are in very good agreement with the existing experimental results (having an average error of better than 2%). This evidence suggests that the proposed rule for developing basis sets allows a reasonable description of the polarized charge cloud. However, since no experimental hyperpolarizability results for the azabenzenes are available currently, the accuracy of our reported values cannot be verified, but comparison of both the α and γ values of this series, with those of benzene (Table II, footnote a) does allow some optimism.

[1] P. Saxe and H. Schaefer III, J. Am. Chem. Soc. **105,** 1760 (1983).
[2] F. Escudero, O. Mó, and M. Yánez, J. Chem. Soc. Perkin Trans. 2 1735 (1983).
[3] P. Birner, H. J. Köhler, and C. Weiss, Chem. Phys. Lett. **27,** 347 (1974).
[4] G. E. W. Bauer and C. Huiszoon, Mol. Phys. **47,** 565 (1982).
[5] B. F. Levine, C. G. Bethea, C. D. Thurmond, R. T. Lynch, and T. L. Bernstein, J. Appl. Phys. **50,** 2523 (1979).
[6] E. F. McIntyre and H. F. Hameka, J. Chem. Phys. **70,** 2215 (1979).
[7] C. A. Nicolaides, M. G. Papadopoulos, and J. Waite, Theor. Chim. Acta **61,** 427 (1982).
[8] M. G. Papadopoulos, J. Waite, and C. A. Nicolaides, J. Chem. Phys. **77,** 2527 (1982).
[9] J. Waite, M. G. Papadopoulos, and C. A. Nicolaides, J. Chem. Phys. **77,** 2536 (1982).
[10] J. Waite and M. G. Papadopoulos, J. Comput. Chem. **4,** 578 (1983); J. Mol. Struct. **108,** 247 (1984).
[11] F. Mulder, G. Van Dijk, and C. Huiszoon, Mol. Phys. **38,** 577 (1979).
[12] F. T. Marchese and H. H. Jaffé, Theor. Chim. Acta **45,** 241 (1977).
[13] J. Maddox, Nature **306,** 311 (1983).
[14] A. D. Buckingham, Adv. Chem. Phys. **12,** 107 (1967).
[15] T. K. Ha, R. Cimiraglia, and M. T. Nguyen, Chem. Phys. Lett. **83,** 317 (1981).
[16] M. P. Bogaard, A. D. Buckingham, M. G. Corfield, D. A. Dunmur, and A. H. White, Chem. Phys. Lett. **12,** 558 (1972).
[17] J. F. Ward and D. S. Elliott, J. Chem. Phys. **69,** 5438 (1978).
[18] M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. **99,** 4907 (1977).
[19] L. Fanfani, M. Tomassini, P. F. Zanassi, and A. R. Zanzari, Acta Crystallogr. Sect. B **31,** 1740 (1975).
[20] M. Martinez-Ripoll and H. P. Lorenz, Acta Crystallogr. Sect. B **30,** 793 (1974).
[21] *Tables of Interatomic Distances and Configurations in Molecules and Ions* (The Chemical Society, London, 1965).
[22] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968).
[23] T. Voegel, J. Hinze, and F. Tobin, J. Chem. Phys. **70,** 1107 (1979).
[24] A. D. Buckingham, M. P. Bogaard, D. A. Dunmur, C. P. Hobbs, and B. J. Orr, Trans. Faraday Soc. **66,** 1548 (1970).
[25] J. F. Ward and C. K. Miller, Phys. Rev. A **19,** 826 (1979).
[26] G. M. Barrow, *Physical Chemistry* (McGraw-Hill, New York, 1966).