

MNDO Semiempirical and 4-31G ab Initio SCF-MO Calculations of Heteroaromatic Compounds

Empar Fos and Jaume Vilarrasa*

Departament de Química Orgànica, Facultat de Química, 08028 Barcelona, Catalonia, Spain

Javier Fernández

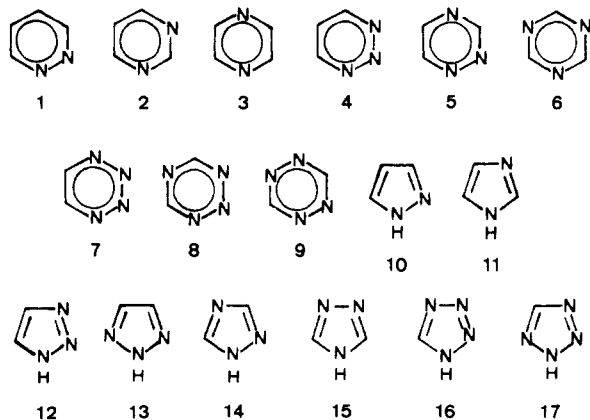
Laboratoire de Chimie Structurale, UA474, Université de Pau, 64000 Pau, France

Received May 21, 1985

The performance of the MNDO method, as far as the energies of azines and azoles are concerned, is critically evaluated after comparing its results with some ab initio calculations at the 4-31G level and with available experimental data. The lone-pair electronic repulsions between the neighboring pyridine-like nitrogens are systematically underestimated by MNDO. Nevertheless, when corrections are introduced, even the relative stabilities of quite complex heterocyclic systems (tetrazolotriazine and tetrazolobenzotriazine tautomers) are predicted with reasonable accuracy.

Semiempirical SCF-MO methods are rather popular within the organic chemists' community since, with a moderate cost, they offer quite reliable results (in specific areas) of either explanatory or predictive value for medium-to-large-sized molecules. Outstanding among which there is the MNDO method of Dewar and Thiel,¹ with parameters now available for the second-period elements and also for Al, Si, P, S, Cl, Br, I, and Sn.² Its utility for searching equilibrium geometries of unusual species before entering them as trial geometries in ab initio calculations is recognized as well. Nevertheless, as any theoretical method, MNDO has its own limitations.^{1,3}

In this connection, it would be useful to evaluate the confidence of the MNDO-calculated energies, geometries, and dipolar moments of heteroaromatic compounds that constitute the most characteristic substructures of many natural products and/or pharmaceutical preparations. In particular, our interest was first focused on polyazaheterocycles such as the diazines (1-3), triazines (4-6), tetrazines (7-9), diazoles (10 and 11), *v*-triazole tautomers (12 and 13), *s*-triazole tautomers (14 and 15), and tetrazole tautomers (16 and 17).



In the original MNDO papers,¹ besides pyridine and pyrrole, pyridazine (1), pyrimidine (2), and pyrazine (3)

Table I. MNDO ΔH_f° Values (in kcal/mol) and Some 4-31G//MNDO Total Energies (in au)^a for Diazines, Triazines, and Tetrazines

compd	MNDO		4-31G/MNDO	
	ΔH_f°	rel energy	total energy	rel energy
1	44.2 ^b	8.7	-262.2370	26.7
2	35.5 ^b	0.0	-262.2795	0.0
3	38.3 ^b	2.8	-262.2718	4.8
4	56.5	15.7	-278.1538	50.0
5	52.4	11.6	-278.1833 ^c	31.4
6	40.8	0.0	-278.2334	0.0
7	71.3	7.4		
8	63.9	0.0		
9	68.9	5.0		

^a 1 au or hartree = 627.5 kcal/mol. ^b See also ref 1b. ^c A 4-31G//STO-3G calculation gives -278.1817 au. See ref 11.

were included. The heats of formation calculated for 1-3 were rather discouraging about the future of MNDO in heterocyclic chemistry, since these molecules were predicted to be ca. 22, 11, and 9 kcal/mol, respectively, more stable than expected. Indeed, these errors are far above the mean absolute error of ca. 6 kcal/mol for the overall MNDO-calculated heats of formation.^{1b} However, pyrazole (10) and imidazole (11), as well as other heterocycles, were found more recently to be well-described by MNDO, since the calculated heats of formation were almost within the range of error of the experimental ΔH_f° values.⁴ Thus, it was thought as a hypothesis that an underestimation of the electronic repulsion between pyridine-like nitrogens and a bad estimation of the energies of six-membered heterocycles might operate together. The last assumption is plausible, since even for pyridine and 3 (with the two nitrogens away) MNDO gives heats of formation lower than expected. Thus, the relative energies within each set of isomers, rather than the heats of formation, have been actually taken into account in the present paper, in order to evaluate mainly the above-mentioned underestimation of the electronic repulsion. This is carried out after comparing the MNDO results⁵ with some ab initio calculations with use of the 4-31G basis set,⁶ with former calculations

(1) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899; (b) 1977, 99, 4907.

(2) See: Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* 1984, 106, 6771 and references therein.

(3) (a) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* 1979, 101, 5558 and references therein (general review). (b) Thiel, W. *Ibid.* 1981, 103, 1413 (open-shell states). (c) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *Ibid.* 1981, 103, 5609. (d) Ford, G. P.; Scribner, J. D. *J. Comput. Chem.* 1983, 4, 594. (e) Olivella, S.; Urpi, F.; Vilarrasa, J. *Ibid.* 1984, 5, 230 (charged species).

(4) Olivella, S.; Vilarrasa, J. *J. Heterocycl. Chem.* 1981, 18, 1189. See also ref 3e.

(5) The MOPAC package (QCPE no. 464) and a IBM 4341/MO 2 computer were used. All equilibrium geometries were determined by minimizing the total energy with respect to all geometrical variables, unless otherwise indicated.

(6) The GAUSSIAN-80 series of programs was used. See: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* 1981, 13, 406.

from others, and with available experimental data. Then, the conclusions arising from these comparisons have been applied to elucidate a conspicuous question related to the azide/tetrazole equilibrium in tetrazolo-*as*-triazines⁷ (i.e., to molecules containing six nitrogen atoms).

Results and Discussion

Experimental ΔH_f° values for the heterocycles reported here can hardly be found in the literature,⁸ except for the diazines (1–3), which are the most studied compounds of the series from a theoretical viewpoint.⁹ Experimentally, 2 and 3 have nearly the same ΔH_f° value and are 20 kcal/mol more stable than 1.^{8a,b} Both MNDO calculations^{1b} and ab initio calculations with a minimal basis set^{9a} reproduce this trend qualitatively, but the values for 1 are calculated to be only 8.7 and 13.6, respectively, above 2. Total energies calculated now (see Table I) by means of the 4-31G program by using MNDO geometries (i.e., 4-31G//MNDO calculations) give 2 and 3 as more stable than 1 by 26.7 and 21.9 kcal/mol, respectively.

In summary, MNDO and minimal-basis set ab initio calculations give too low energy values for 1, whereas the gaps among these azines calculated by 4-31G//MNDO appear to be a bit larger than the experimental ones.¹⁰

Is the above-mentioned MNDO overestimation of the stability of molecules with two neighboring nitrogens systematically maintained along the azine series?

Triazines. The heats of formation calculated by MNDO and the total energies calculated by 4-31G//MNDO for 1,2,3-triazine or *v*-triazine (4), 1,2,4-triazine or *as*-triazine (5), and 1,3,5-triazine or *s*-triazine (6) are shown in Table I. Although ΔH_f° for 6 is known (54.0 kcal/mol),^{8c} there are no experimental values regarding the relative stabilities of these molecules, so we assumed that, as occurred in diazines, the 4-31G//MNDO results may be more realistic than the MNDO ones.¹¹

Qualitatively, the same trend is observed in any of the two computational methods: the triazine with three vicinal nitrogens (4) is more unstable than that with two vicinal nitrogens (5), and this one is more unstable than 6. Indeed, this order is intuitively correct, bearing in mind the thermal stability and the large number of known *s*-triazine derivatives (and the easy trimerization of X—C≡N to) and, on the opposite site, the scarce number of *v*-triazines reported so far in the literature. However, MNDO fails to give an accurate quantitative measure of their thermodynamic differences.

Table II. MNDO ΔH_f° Values and ab Initio Relative Energies (all in kcal/mol) for Triazoles and Tetrazoles

compd	MNDO		ab initio rel energies		
	ΔH_f°	rel energy	4-31G//MNDO ^a	min basis ^b	STO-3G//INDO ^c
12	50.7	9.7		11.0	18.9
13	57.0	16.0		9.7	15.1
14	44.6	3.6		0.0	0.0
15	41.0	0.0		2.7	5.1
16	55.0	0.0	1.6	0.0	0.0
17	59.2	4.2	0.0	0.7	0.2

^a 4-31G//MNDO total energies for 16 and 17 equal to -256.3101 and -256.3126 au, respectively. A 4-31G//STO-3G calculation of 16 gives -256.3136 au (i.e., only 2.2 kcal/mol are gained using the STO-3G instead of the MNDO geometry). ^b See ref 16. ^c See ref 18.

Taking into account what occurs in the diazines, a correction term of 10–12 kcal/mol could be suggested to compensate the MNDO underestimation of the lone-pair electronic repulsion between vicinal nitrogens; so, the resulting estimated relative energies for 4 and 5 would be 15.7 + 2 × 10 (or 12) = 36–40 kcal/mol and 11.6 + 1 × 10 (or 12) = 22–24 kcal/mol, which seem reasonable.

As far as calculated dipolar moments are concerned, the relative order is also coincident, but again the ab initio calculations give larger values (6.09, 2.97, and 0.0 D for 4 to 6, respectively) than MNDO ones (4.60, 2.28, and 0.0 D, respectively).

Tetrazines. The MNDO-calculated heats of formation for 1,2,3,4-tetrazine (7), 1,2,3,5-tetrazine (8), and 1,2,4,6-tetrazine (9) are also shown in Table I.¹² Dipolar moments are found to be 4.32, 2.56, and 0.0 D, respectively. There is the feeling that all these values may be relatively correct though too low; however, the scarcity of experimental data for tetrazines¹³ suggests to deal with the subject with caution.

Using the same correction as above, the estimated relative energies for 7/8/9 would be 17–19 to 0 to 5 kcal/mol.

Triazoles. Tautomeric forms of *v*-triazole (12 and 13) and *s*-triazole (14 and 15) are compared in Table II. The *s*-triazole arrangements are predicted to be more stable than the two *v*-triazole (i.e., vicinal) arrangements by all known calculations. However, as compared to ab initio calculations, MNDO gives too low ΔH_f° values for 12 and 15; the alternative view, that the MNDO energies of 13 and 14 are too high, can be ruled out taking into account that the calculated ΔH_f° for 14 agrees perfectly, as in the case of imidazole and pyrazole,⁴ with its estimated experimental value of 46 kcal/mol.¹⁴ Going further, if a relative correction term of 8 to 10 kcal/mol is admitted for azoles with two neighboring pyridine-like nitrogens,¹⁵ the MNDO

(7) For leading references, see: (a) Goodman, M. M.; Atwood, J. L.; Carlin, R.; Hunter, W.; Paudler, W. W. *J. Org. Chem.* **1976**, *41*, 2860. (b) Goodman, M. M.; Paudler, W. W. *Ibid.* **1977**, *42*, 1866. (c) Messmer, A.; Hajós, G.; Tamás, J.; Neszmélyi, A. *Ibid.* **1979**, *44*, 1823. (d) Castellón, S.; Meléndez, E.; Pascual, C.; Vilarrasa, J. *Ibid.* **1982**, *44*, 3886. (e) Castellón, S.; Vilarrasa, J. *Ibid.* **1982**, *47*, 3168. (f) Hajós, G.; Messmer, A.; Neszmélyi, A.; Párkányi, L. *Ibid.* **1984**, *49*, 3199.

(8) (a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) Nabavian, M.; Sabbah, R.; Chastel, R.; Laffitte, M. *J. Chim. Phys.* **1977**, *74*, 115. (c) Bystroem, K. *J. Chem. Thermodyn.* **1982**, *14*, 865.

(9) For recent ab initio calculations, see: (a) Palmer, M. H.; Simpson, I. Z. *Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1983**, *38a*, 415. (b) Price, S. L.; Stone, A. J. *Chem. Phys. Lett.* **1983**, *98*, 419. (c) Pang, F.; Pulay, P.; Boggs, J. E. *J. Mol. Struct.: THEOCHEM* **1982**, *88*, 79. (d) Niessen, W. V.; Kraemer, W. P.; Diercksen, G. H. F. *Chem. Phys.* **1979**, *41*, 113. (e) Palmer, M. H.; Gaskell, A. J.; Findlay, R. H. *J. Chem. Soc., Perkin Trans. 2* **1974**, 778. (f) Almlöf, J.; Roos, B.; Wahlgren, U.; Johnsen, H. *J. Electron. Spectrosc. Relat. Phenom.* **1973**, *2*, 51.

(10) Other ab initio calculations, with two notable exceptions,^{9b,d} give erratic or exaggerated relative energies.

(11) By the way, a 4-31G calculation of 5 with geometry optimization at the STO-3G level affords a total energy value of -278.1817 au (i.g., ca. 1 kcal/mol is "lost" in using STO-3G instead of MNDO equilibrium geometries).

(12) For recent theoretical works on hexazine, see: (a) Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 1760. (b) Huber, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 64. (c) Ha, T. K.; Cimiriaglia, R.; Nguyen, M. T. *Chem. Phys. Lett.* **1981**, *83*, 317. See also references therein.

(13) Only the crystalline structure of 9 has been reported, to our knowledge.

(14) After adding to the experimental value of 26.1 ± 0.2 kcal/mol for the solid (Aleksandrov, Y. I.; Osipova, T. R.; Yushkevich, V. F. *Termodin. Org. Soedin.* **1982**, *42*; *Chem. Abstr.* **1983**, *99*, 37905u) an estimated heat of sublimation of ca. 20 kcal/mol, the heats of sublimation of 10 and 11 are 16.5 and 17.8 kcal/mol, respectively (Sabbah, R. *Thermochim. Acta* **1980**, *41*, 33), and that of 16 is 23.3 kcal/mol.^{8a}

(15) The electronic repulsion between the corresponding lone pairs must be a bit smaller in five-membered rings than in six-membered rings because of the smaller bond angles. Furthermore, since the localization of single and double bonds is more significant in azoles, it is believed that the correction applied to 12, with a shorter N2–N3 bond, should be a bit larger (10 kcal/mol) than that applied to 15 (about 8 kcal/mol), with a longer N3–N4 bond.

calculations shown in Table II are put in order with the other ones (the four figures on the top of the third column of Table II "should be" ca. 16, 12, 0, and 4, instead of ca. 10, 16, 4, and 0).

Regarding the position of the tautomeric equilibria ($12 \rightleftharpoons 13$ and $14 \rightleftharpoons 15$) there is a lot of experimental information, either in gas phase or in solution. For instance, photoelectron spectroscopy indicates that 13 predominates largely (>99%) over 12, and that 14 predominates largely (ca. 100%) over 15¹⁶ (as predicted by ab initio calculations and "corrected" MNDO results). On the other hand, the ¹⁵N NMR spectra of $12 \rightleftharpoons 13$,¹⁷ either in CHCl₃ or Me₂SO, indicate that in the concentrated solutions in which such spectra are registered both tautomers have nearly the same energy, but that of $14 \rightleftharpoons 15$ indicates that 14 still predominates (95%) in Me₂SO. The dipolar moment differences can qualitatively explain these changes, since MNDO predicts 4.03 and 0.24 D for 12 and 13, respectively, and 2.67 and 5.27 D for 14 and 15, respectively.¹⁸ Because of the very small μ_D value of 13, energy of solvation favors the intrinsically more unstable 12 enough to predominate. By contrast, it can be thought that the polarity difference between 14 and 15 does not suffice to "invert" the equilibrium position in passing from the gas phase to condensed phase.

Tetrazoles. By several reasons, the two tautomers of tetrazole—1*H*-tetrazole or 1,2,3,4-tetrazole, 16, and 2*H*-tetrazole or 1,2,3,5-tetrazole, 17—attracted our attention more than any other set of heterocyclic isomers. The experimental ΔH_f° value for tetrazole (g) is 80.0 ± 1.1 kcal/mol,^{8a} whereas the MNDO calculated values for 16 and 17 are 20 or more kcal/mol below (see Table II). Thus, as expected, overestimation of the stability of polynitrogenated structures appears again. What is more important is that 17 largely predominate in the gas phase;^{16,20} thus, our 4-31G//MNDO and the STO-3G//INDO results of Catalan et al.¹⁸ seem quite confident. On the other hand, the already established correction term of 8 to 10 kcal/mol for each destabilizing interaction¹⁵ should be applied to the MNDO results to reach reliable energies; in such a case, the relative energy of 16 turns out $0 + 10 + 8 = 18$ and that of 17 becomes $4 + 10 = 14$ (i.e., 16 is found 4 kcal/mol above 17 instead of vice versa.)

In polar solvents, equilibrium $16 \rightleftharpoons 17$ is, however, shifted in favor of 16,^{17,18} which is accounted for by the higher dipolar moment of 16 (5.10 D according to

MNDO)²¹ as compared with that of 17 (1.90 D according to MNDO).²¹

Effect of the N–N Bond Length. It has been shown so far that 4-31G//MNDO relative energies match the available experimental data, even in those cases in which MNDO fails to reproduce the expected energy order. Thus, the MNDO underestimation of the destabilizing factors that operate in polynitrogenated heterocycles seems intrinsic to the method.

Nevertheless, a look to the calculated equilibrium geometries indicated that the N–N bond lengths of vicinal pyridine-like nitrogens were short, lying usually between 1.27 and 1.29 Å, whereas the experimental N–N bond distance in 1 (from microwave spectra) is 1.330 Å,²³ in 9 (from the X-ray structure) is 1.321 Å, and so on.²⁴ The calculated NNC bond angles were also larger than the experimental ones, but it may be partially related to the short N–N distances. To summarize, MNDO predicts structures slightly distorted—more flat than the experimental ones—near the nitrogen atoms. What happens if such distortions are avoided in the MNDO calculations?

The bond lengths of azines 1, 4, 5, 7, 8, and 9 were calculated again, but their N–N bond lengths were fixed to 1.330 Å, with all the remaining geometric parameters being optimized in the usual way. The bond lengths of tautomers 16 and 17 were also calculated after setting r (N2–N3) of 16 and 17 equal to 1.300 Å and r (N3–N4) of 16 equal to 1.350 Å. The resulting ΔH_f° values were the following: 45.9 kcal/mol (instead of 44.2 kcal/mol)^{1b} for 1; 60.4 (instead of 56.5) for 4; 54.2 (instead of 52.4) for 5; 75.8 (instead of 71.3) for 7; 67.9 (instead of 63.9) for 8; 74.5 (instead of 68.9) for 9; 56.0 (instead of 55.0) for 16; and 60.0 (instead of 59.2) for 17. Obviously, these changes are not significant,²⁵ i.e., geometry corrections do not arrange the shortcomings of MNDO very much. This agrees with the above-mentioned fact (cf. ref 11 and Table II) that 4-31G//MNDO and 4-31G//STO-3G calculations give nearly the same energies. In other words, the above statements about the systematic, intrinsic MNDO underestimation of some destabilizing factors are well founded.

As known, MNDO is based in the NDDO approximation^{1a} (in which only the diatomic differential overlap is neglected), whereas most semiempirical methods are based in the more simplified CNDO and INDO approximations (in which additional electron repulsion integrals are ruled out). However, according to their authors,¹ MNDO takes into account the directional effects in the two-center electron–electron repulsions and core–electron attractions. Thus, it is understandable that MNDO improves MINDO/3, for instance, as far as molecules with N–N bonds are concerned.^{1b} Thus, it can be admitted that the performance of MNDO in calculating heterocyclic structures should be superior to any other semiempirical method. But it systematically fails for molecules with close pyridine-like nitrogens, indicating that the approximations or simplifications of the method are not sufficiently com-

(16) Palmer, M. H.; Simpson, I.; Wheeler, J. R. *Z. Naturforsch., A: Phys. Phys. Chem., Kosmophys.* 1981, 36a, 1246 and references therein.

(17) (a) Wofford, D. S.; Forkey, D. M.; Russell, J. G. *J. Org. Chem.* 1982, 47, 5132. (b) Bojarska, E.; Stefaniak, L.; Witanowski, M.; Hamdi, B. T.; Webb, G. A. *Magn. Res. Chem.* 1985, 23, 166.

(18) See also Catalán, J.; Paz, J. L. G.; Yáñez, M.; Elguero, J. *Chem. Scr.* 1984, 24, 84 and references therein. In this paper, which appeared when most of the present work was accomplished, STO-3G//INDO calculations on the azole series were reported. The dipolar moments calculated for the four triazoles agree with ours: 4.16, 0.16, 2.88, and 4.64 D for 12–15, respectively.

(19) For calculations on pentazole, see: (a) Roberts, J. D. "Notes on Molecular Orbital Calculations"; Benjamin: New York, 1962. J. V. recognizes with pleasure that the reading of this book and its pentazole treatment was what developed his interest for theoretical chemistry ca. 12 years ago. (b) The MNDO-calculated heat of formation of pentazole is 66.0 kcal/mol, a value below that calculated for hydrogen azide (73.0 kcal/mol)^{1b} and far below that for the zigzag pentazene structure (101.2 kcal/mol). It is obvious from these data (unpublished work taken from a lecture given in the biennial Spanish organic chemist's meeting held at Ronda on April 1979) that MNDO overestimates the stability of pentazole in the same way as it does for the polyazaheterocycles studied in this paper. (c) Sana, M.; Leroy, G.; Nguyen, M. T.; Elguero, J. *Nouv. J. Chim.* 1979, 3, 607. See also ref 18.

(20) Razynska, A.; Tempczyk, A.; Malinski, E.; Szafranek, J.; Grzonska, Z.; Hermann, P. *J. Chem. Soc., Perkin Trans. 2* 1983, 379.

(21) 4-31G//MNDO gives 6.25 and 2.35 D, respectively, STO-3G//INDO^{1b} gives 5.22 and 2.23, and LCGO²² gives 5.17 and 2.54. Experimental values, either in the gas phase or in dioxane solution, agree perfectly with these calculations.^{18,22}

(22) Palmer, M. H.; Findlay, R. H.; Gaskell, A. J. *J. Chem. Soc., Perkin Trans. 2* 1974, 420.

(23) Alménningen, A.; Björnson, G.; Ottersen, T.; Seip, R.; Strand, T. *G. Acta Chem. Scand.* 1977, 31, 63.

(24) Cf. Wheatley, P. J. "Physical Methods in Heterocyclic Chemistry"; Katritzky, A. R., Ed.; Academic Press: New York, Vol. V, 1972.

(25) Dipolar moments do not practically change, indeed.

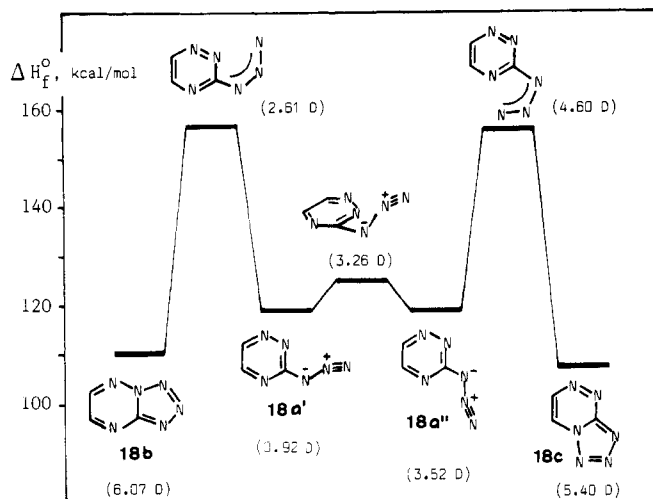
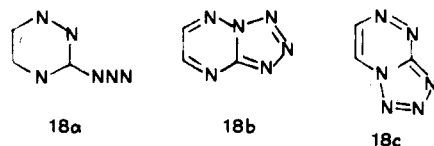


Figure 1. MNDO-calculated heats of formation of the isomers and transition states involved in the 18a/18b/18c equilibrium. Calculated dipolar moments are within parentheses.

pensated by the parametrization.²⁶

Application of MNDO to an Azide/Tetrazole Equilibrium. As justified above, one must add 10–12 kcal/mol to the MNDO-calculated energies of azides, for each pair of vicinal nitrogen atoms, in order to get reasonable relative energies for isomeric compounds. Similarly, the correction term must be 8 or 10 kcal/mol in the azole series. With these assumptions in hand, we focused our attention on a controversial ternary azide/tetrazole equilibrium, involving the *as*-triazine ring, which has arisen in recent years mainly in this journal:⁷ whereas simple 3-azido-*as*-triazines (see 18a) cyclize on N2 to give the



tetrazolo[1,5-*b*]-*as*-triazine arrangement (18b), 3-azido-*benzo-as*-triazines (19a) cyclize in polar solvents either on N2 or N4 affording ternary equilibrium mixtures (19a/19b/19c) in which the tetrazolo[5,1-*c*]benzo-*as*-triazine arrangements (19c) often predominate, although it depends on the substituents;^{7d} in the naphtho series, it has been shown^{7e,f} that tetrazole arrangement **b** (cyclization taking place on N2) largely predominates in naphtho[2,1-*e*]-*as*-triazine and naphtho[1,2-*e*]-*as*-triazine, while tetrazole arrangement **c** (cyclization occurring on N4) does it in naphtho[2,3-*e*]-*as*-triazine. Could MNDO reproduce (and help with the interpretation of) these experimental facts?

Figure 1 shows the calculated heats of formation concerning the 18a/18b/18c isomerizations; the corresponding dipolar moments are indicated within parentheses. The two azide conformers, with all the atoms in the same plane,

(26) There are some possibilities for anybody interested in theoretical aspects of either open-chain or heterocyclic polynitrogenated compounds: (i) to forget semiempirical methods and use reliable *ab initio* calculations (i.e., with large basis sets); this is at present prohibitive for most heterocyclic natural products and related heteroaromatic compounds; (ii) to wait for or try a new MNDO parametrization which, for instance, included some imines, diazenes, and/or azines as standard molecules, since in the original parametrization only hydrazine was entered; this may compensate, at least partially, the intrinsic "defects" of the NDDO approximation; (iii) to use the present MNDO method and introduce suitable correction terms, provided that the "errors" were systematic, as demonstrated in this paper; for practical reasons, this seems advisable.

Table III. MNDO Results^a for Tautomers 19, 21, 23, and 24

compd	ΔH_f°	corrected rel energies	μ_D
19a'	134.2	0	1.81
19a''	133.6	0	3.53
19b	130.8	3–5	7.46
19c	116.5	0	6.47
21a'	67.7	2–4	1.00
21a''	67.6	2–4	2.38
21b	58.3	0	5.90
21c	56.8	9–11	4.87
23a'	64.6	1–3	1.22
23a''	65.3	1–3	4.19
23b	55.7	0	5.88
23c	56.8	11–13	4.86
24ab	72.7	5–7	3.05
24ac	84.4	6	3.98
24b	59.5	0	3.42
24c	60.3	0	5.07

^aHeats of formation and relative energies in kcal/mol, dipolar moments in Debyes.

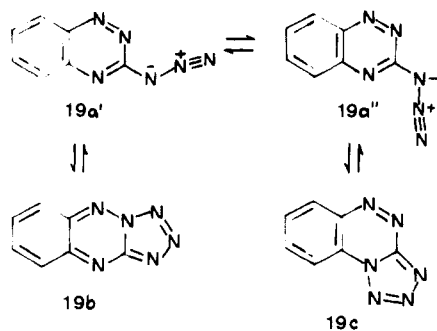
have identical energy (119.2 and 119.3 kcal/mol) but very different μ_D values; their interconversion barrier by rotation around the C3-N α bond (i.e., with N β and N γ out of the plane) is only 5.8 kcal/mol, whereas the barrier associated with the inversion of N α (i.e., with C3, N α and N β in straight line) is 40 kcal/mol. The transition states for cyclizations 18a' → 18b and 18a'' → 18c are located at 156.7 and 156.0 kcal/mol, respectively, so that no significant kinetic advantages should be expected for any of the two possible cyclizations. Tetrazole form 18c is predicted to be more stable than 18b (107.5 vs. 110.1 kcal/mol) but not as polar.

Applying the correction terms established before,²⁷ the relative energies of the species involved would be as follows: 18b, 0 kcal/mol; 18a', 1–3 kcal/mol; 18a'', 1–3 kcal/mol; and 18c, 8–10 kcal/mol. In other words, in the gas phase 18b may be the major tautomer (although 18a'/18a'' may be detected), and in the condensed phase, especially in solvents of high dipolar moment, 18b should predominate even more because of its higher polarity. This actually happens with Me₂SO.

It is worth noting that 4-31G//MNDO calculations of 18b and 18c give total energies of -440.5775 and -440.5631 au, respectively, so that 18b turns out to be 9.1 kcal/mol more stable than 18c. The respective dipolar moments are 7.57 and 6.72 D. Thus, there is a good agreement between the "empirically corrected" MNDO energies and the *ab initio* ones and between the predicted relative polarities.

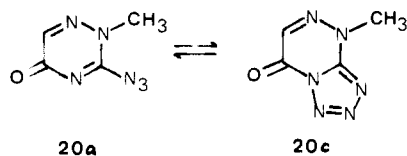
The equilibrium among 3-azidobenzo-*as*-triazine (19a), tetrazolo[1,5-*b*]benzo-*as*-triazine (19b), and tetrazolo[5,1-*c*]benzo-*as*-triazine (19c) has also been studied by MNDO. Looking either at the ΔH_f° values or the corrected energies of the 18b = 18a' = 18a'' = 18c and 19b = 19a' = 19a'' = 19c (Table III) sets, it is deduced that something stabilizes 19c and destabilizes 19b in relation to 18c and 18b, respectively. In our opinion,^{7d,e} the stabilizing factor is the *N*-phenyltetrazole substructure of 19c, and the destabilizing factor of 19b is its quinone-like structure; azido-triazines would cyclize on N2 rather than on N4 in order to avoid the in-plane lone-pair electronic repulsion of the pyridine-like nitrogens, but the relative aromatic character of the resulting polycycles can play an opposite role in some derivatives.

(27) No correction is required for the azide group, since MNDO describes it quite well. See ref 1b and Olivella, S.; Vilarasa, J. J. *Heterocycl. Chem.* 1979, 16, 685.



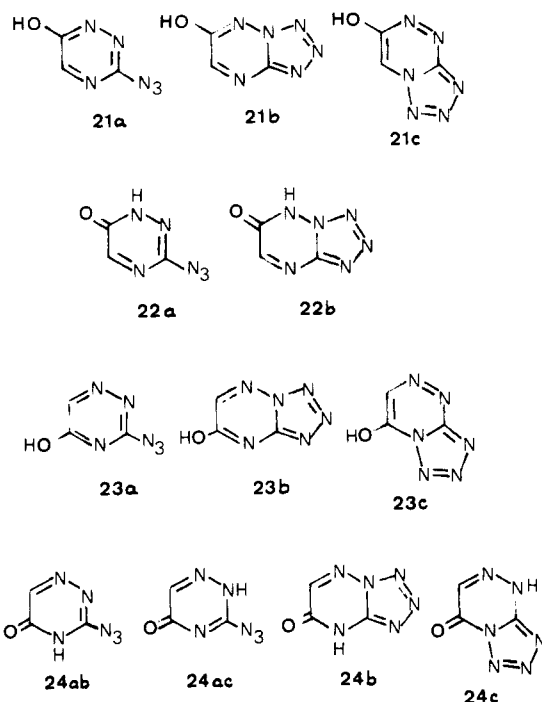
It is also remarkable that the corrected relative energies of tautomers **19** are so close, giving rise to the unusual ternary equilibria observed in solution.²⁸ In fact, the less stable tautomer (**19b**) is the more polar one, so that its percentage in passing from the gas phase to CHCl_3 , acetone, Me_2SO , and the solid state should increase more than any other tautomer, and this occurs indeed along the series just mentioned.^{7d} Another curious result, never reported before to our knowledge, is the polarity difference between azide conformers (**18a'** vs. **18a''**, **19a'** vs. **19a''**), which, bearing in mind the low interconversion barrier between them, suggests that the azide form may show a "chameleonic" behavior, being able for instance to appear as the major tautomer in apolar solvents and remain or "survive" in the most polar solvent. This idea may be of general interest and application.

How does one detect or trap a **18c** derivative? All the simple 3-azido-*as*-triazines studied so far^{7a,b} cyclize partially or totally, depending on the conditions, on N2. Only when N2 is blocked (see **20a**), is cyclization on N4 (**20c**) observed under suitable conditions.^{7b}



Ruling out that trivial situation, what kind of substituents on C4 or C5 could allow one to detect tautomer **c**? Attention was focused on the structures **21** and **23**, in which a π -donor substituent such as the hydroxy group is present²⁹ and on their possible prototropic tautomers (**22** and **24**, respectively). Intuitively, **24c** should be a good candidate since the in-plane lone-pair N1-N2 repulsion is avoided; **24c** should be even better in this connection than the anion (**25c**) arising from the removal of the acidic proton of tautomers **23c** and **24c**.

MNDO results (see Table III) show no significant changes for the **21a/21b/21c** and **23a/23b/23c** series with regard to the **18a/18b/18c** series, either in their relative energies or in their dipolar moments.³⁰ But this is not true for compounds **24**. Almost the same intrinsic stability should be expected for both tetrazole forms; furthermore, in polar solvents **24c** should be favored over **24b**. It was reported some years ago^{7b} that **24b** was the only tautomer present in Me_2SO . In view of the calculations and arguments shown here, the question may be posed of whether **23b**—the most stable³¹ and polar of all the involved



tautomers—instead of **24b** could not be the major species really observed. Anyway, of course, the rule about the preference of the cyclization on N2 in simple azido-*as*-triazines is obeyed.

Conclusions

It has been shown that the MNDO-calculated heats of formation of heterocyclic azines are too low or are suspected—there is a lack of experimental data—to be too low, mainly when two or more nitrogens are vicinal. By contrast, the heats of formation calculated for azoles are reliable, except for the cases in which, as above, two or more pyridine-like nitrogens are vicinal. The systematic underestimation of the corresponding N-N electronic repulsions, which is inherent in the NDDO approximation, is also reflected in the N-N bond distances and CNN bond angles but not at all or not so much in the remaining geometrical parameters and the charge distributions.

As far as the relative energies of isomers are concerned, 4-31G//MNDO (and 4-31G//STO-3G) calculations fit in with the available experimental data, whereas MNDO needs some corrections: 10–12 kcal/mol for each pair of neighboring nitrogens in the azines and 8 or 10 kcal/mol, depending on the N-N bond order, for the same concept in the azoles.

When these corrections are applied to MNDO-calculated energies of complex heterocyclic molecules (tetrazolotriazine systems), for which at least a reasonable amount of empirical data is known, satisfactory agreement is always achieved.

Acknowledgment. Thanks are due to the Laboratori de Càlcul de la Universitat de Barcelona for providing computer time. J. V. also thanks Dr. S. Olivella for making available his personal copies of MNDO programs. Prof. M. H. Palmer is also acknowledged for affording us valuable information.

(28) As a matter of fact, it should be "quaternary equilibria", but the very rapid $19a' \rightleftharpoons 19a''$ interconversion by rotation precludes the NMR detection of both azide tautomers.

(29) The hydroxy group is used as a model for the OMe group.

(30) Compounds **22** were not calculated for obvious reasons: a "normal", nitrogen-protonated **22c** structure can not be drawn or, in other words, **22c** is **21c**.

(31) This is, however, a controversial point. According to some authors (Buda, A.; Sygula, A. *J. Mol. Struct.: THEOCHEM* 1983, 92, 255. Mirek, J.; Sygula, A. *Ibid.* 1981, 86, 85 and references therein) both the MNDO and ab initio methods overestimate the stabilities of the "hydroxy" tautomers of pyridine in relation to the "keto" tautomers.

Registry No. 1, 289-80-5; 2, 289-95-2; 3, 290-37-9; 4, 289-96-3; 5, 290-38-0; 6, 290-87-9; 7, 290-42-6; 8, 592-59-6; 9, 290-96-0; 12, 288-36-8; 13, 288-35-7; 14, 288-88-0; 15, 63598-71-0; 16, 288-94-8; 17, 288-95-9; 19a, 69365-63-5; 19b, 69365-64-6; 19c, 50275-24-6; 21a, 98858-73-2; 21b, 98858-74-3; 21c, 98858-75-4; 23a, 98900-92-6; 23b, 98900-91-5; 23c, 98858-76-5; 24ab, 98921-31-4; 24ac,

61788-15-6; 24b, 61788-17-8; 24c, 98858-77-6.

Supplementary Material Available: MNDO equilibrium geometries for all the reported compounds and STO-3G equilibrium geometries for 5 and 16 (4 pages). Ordering information is given on any current masthead page.

The Photochemistry of Bis(2,2-diphenylvinyl) Ether: A Search for the 3-Oxa-di- π -methane Rearrangement

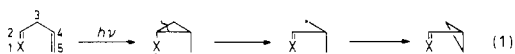
Waldemar Adam,*† Albrecht Berkessel,†‡ Knut Hildenbrand,§ Eva-Maria Peters,|| Karl Peters,|| and Hans Georg von Schnering||

Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-8700, Würzburg, FRG, Max-Planck-Institut für Strahlenchemie, Stiftstr. 34, 4330 Mülheim, FRG, and Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, FRG

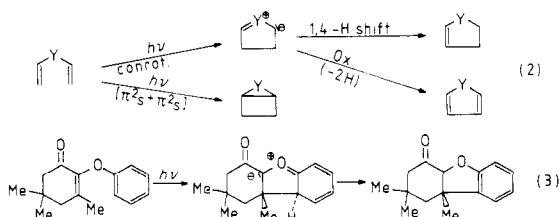
Received July 8, 1985

A convenient synthesis for bis(2,2-diphenylvinyl) ether (**1a**) from diglycolic acid via dehydration of 2,2'-oxybis(1,1-diphenylethanol) (**3a**) is described. The solution photochemistry of divinyl ether **1a** derives from its singlet π, π^* -state and parallels that of the unsubstituted divinyl ether (**1d**) and that of furan in the gas phase. Formation of a singlet $D_{\sigma, \pi}$ vinyl-vinyloxy radical pair is the primary photoreaction ($\Phi_{-S} = 0.12-0.19$). All photoproducts can be convincingly rationalized from this initial radical pair. For example, cage recombination affords 2,2,4,4-tetraphenyl-3-butenal (**13**) as the main product. The mechanistic interpretations are based on results from product studies, photo-CIDNP and crossover experiments. The triplet excited state of divinyl ether **1a** was found to be inert toward decomposition. *trans,trans*-Bis(2-phenylvinyl) ether (**1c**) could be prepared from *trans,trans*-1,4-diphenyl-1,3-butadiene via epoxidation of its Diels-Alder adduct with bis(2,2,2-trichloroethyl) azodicarboxylate and thermal denitrogenation of the corresponding azo compound. The divinyl ether **1c** readily *cis*-*trans* isomerizes upon triplet sensitization, thus implicating *cis*-*trans* isomerization as the deactivation mode of triplet divinyl ether **1a**. 3-Oxa-di- π -methane reactivity of divinyl ether **1a** could not be observed. This result is interpreted in terms of Zimmerman's formalism of bond-order control. Irradiation of the authentic vinyloxirane **7** resulted in the photoextrusion of diphenylcarbene affording 3,3-diphenylpropenal. The intermediacy of the corresponding carbonyl ylide **14** was established by low-temperature UV spectroscopy.

The di- π -methane rearrangement¹ (eq 1, X = CR₂) has been shown to be one of the most ubiquitous reactions in organic photochemistry. Substitution of carbon by heteroatoms in the 1,4-pentadiene chromophore gave rise to the analogous oxa-^{1,2a} (eq 1, X = O) and aza-³ (eq 1, X = NR) di- π -methane reactions. However, other reaction



modes have been possible as well.^{4,5} Replacement of the sp³ carbon in the 3-position by heteroatoms such as O, S, N, Se,⁶ or B^{7,8} afforded so far only inactive di- π -methane systems. Ring closure to five-membered heterocycles or (2 + 2) cycloadditions to bicyclic products were documented as the most prominent reaction pathways (eq 2).



In most of the heterosystems of this type that have been investigated⁶, aromatic rings provided at least one active

π -bond of the 1,4-diene chromophore. An example is the photocyclization of 2-phenoxy-1,5,5-trimethylcyclohexene-3-one⁹ (eq 3). To the best of our knowledge, no detailed examinations of the photolytic behavior of divinyl ethers in solution have been reported. Previous work was concerned with the gas-phase flash photolysis of the parent divinyl ether (**1d**).¹⁰ Vinyl and vinyloxy radicals were formed in the primary step (eq 4). Tetraphenyldioxin (**2**) proved to be photochemically inert.¹¹

Thus, we found it worthwhile to prepare the hitherto unknown bis(2,2-diphenylvinyl) ether (**1a**) and investigate

(1) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* 1973, 73, 531.

(2) (a) Schuster, D. I. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 167.

(b) To distinguish between the various heterosubstituted di- π -methane rearrangements, we suggest to use the usual IUPAC rule for specifying the replaced carbon atom by the appropriate numeric prefix, e.g., the common oxa-di- π -methane rearrangement (ODPM) would herewith be called the 1-ODPM and the present case the 3-ODPM. This nomenclature replaces the previously defined oxydi- π -methane designation for the present 3-ODPM rearrangement (cf.: Adam, W.; Berkessel, A.; Krimm, S. *Tetrahedron Lett.* 1985, 26, 619).

(3) Armesto, D.; Martin, J. A. F.; Pérez-Ossorio, R.; Horspool, W. M. *Tetrahedron Lett.* 1982, 23, 2149.

(4) Armesto, D.; Gallego, M. G.; Pérez-Ossorio, R.; Horspool, W. M. *Tetrahedron Lett.* 1983, 24, 1089.

(5) Armesto, D.; Ortiz, M. J.; Pérez-Ossorio, R.; Horspool, W. M. *Tetrahedron Lett.* 1983, 24, 1197.

(6) Leone, A. A.; Mariano, P. S. *Rev. Chem. Intermed.* 1981, 4, 81.

(7) Ramsey, B. G.; Anjo, D. M. *J. Am. Chem. Soc.* 1977, 99, 3182.

(8) Sobieralski, T. J.; Hancock, K. G. *J. Am. Chem. Soc.* 1982, 104, 7533.

(9) Schultz, A. G.; Erhardt, J.; Hagmann, W. K. *J. Org. Chem.* 1977, 42, 3458.

(10) McFadden, K. O.; Currie, C. L. *J. Chem. Phys.* 1973, 58, 1213.

(11) George, M. V.; Kumar, C. V.; Scaiano, J. C. *J. Phys. Chem.* 1979, 83, 2452.

* Universität Würzburg.

† Fonds der Chemischen Industrie Doctoral Fellow, 1982-1984.

§ Max-Planck-Institut für Strahlenchemie.

|| Max-Planck-Institut für Festkörperforschung.