formers from the molecule to the radical.

Corroborative evidence for our conclusions is based on the observation of the hydrogen hyperfine splitting (hfs) constants in the light of the W empirical rule. It has been in fact recognized that in σ-radicals the largest hfs are expected at the positions corresponding to the extreme of a zigzag (or W) chain of bonds, having the orbital of the unpaired electron at the other extreme.[47] In the case of the S,O-syn conformer of 2-thenoyl radical, **5**, this rule predicts the largest hfs to be at position 5, in agreement with the experimental assignment obtained after methyl substitution (see radicals **6** and **7** in Chart I). Similarly, in the O,O-syn conformer of the 2-furoyl radical, **1a**, the largest hfs comes from position 5 (see the 5-methyl-substituted radical **2**), again in agreement with the zigzag rule; it is therefore reasonable to assume[51] the largest hfsc to be at position 4 in the O,O-anti conformer, **1b**.

Experimental Section

The aldehydes used in this work were purified by distillation immediately before the experiments: without this precaution nonreproducible results were obtained.

Di-*tert*-butyl peroxide was passed through alumina so as to remove traces of di-*tert*-butyl hydroperoxide.

The kinetics of H-atom abstraction were performed by using a laser flash photolysis apparatus, equipped with optical detection with a pulsed Molectron nitrogen laser (337.1 nm, 8 ns, 10 mJ). This apparatus and associated experimental procedures have been described elsewhere.[52] The solvent used in the laser flash photolysis experiments was a 1:2 (v/v) mixture of benzene and di-*tert*-butyl peroxide; all the samples were carefully deoxygenated.

EPR spectra were recorded on a Varian E-104 instrument; the samples were photolyzed directly in the cavity of the spectrometer with a 500-W mercury lamp as irradiating source. Measurement of the bimolecular decay kinetics was carried out by generating the radicals with the repetitive pulses of the same Molectron nitrogen laser. The time profile of the growth and decay of the radical signal (time-resolved EPR spectroscopy) was obtained by feeding the unfiltered output of the EPR spectrometer into a Nicolet 1170 signal averager. Radical concentrations were measured with a method that has been described previously.[26]

The NMR spectra were recorded with a Varian XL-100 instrument equipped with a thermocouple inserted in the probe before or after each experiment. The ^{13}C spectra (25.16 MHz) were obtained in the FT mode (10-mm tubes) on an external Fluorine lock device. The H-1 spectra (100 MHz) were obtained in the FT mode with use of coaxial 5-mm tubes: deuterated acetone in the inner tube provided the signal for the internal deuterium lock.

Acknowledgment. Part of the work described here was carried out during the stay of one of us (L.L.) in Ottawa as a guest of the National Research Council of Canada. Grateful thanks are due to Drs. K. U. Ingold and J. C. Scaiano (N.R.C., Chemistry Division) for generously allowing the use of their apparatus and for helpful comments and discussions. The financial support of the Italian Ministry of Public Education is also acknowledged.

Registry No. 1a, 83323-06-2; **2**, 90866-67-4; **3**, 90866-68-5; **4**, 90866-69-6; **5**, 90866-70-9; **6**, 90866-71-0; **7**, 90866-72-1; **8**, 90866-73-2; *t*-BuO·, 3141-58-0; CH_3CH_2CHO, 123-38-6; $HC(O)NMe_2$, 68-12-2; HC(O)OEt, 109-94-4; PhCHO, 100-52-7; perdeuteriobenzaldehyde, 17901-93-8; 2-furancarboxaldehyde, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3.

Supplementary Material Available: Tables giving detailed kinetic data (11 pages). Ordering information is given on any current masthead page.

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(50) Perkins, C. W.; Martin, J. C. Arduengo, A. J.; Lau, W.; Angria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753–7759.

(51) INDO calculations carried out for the S,O-anti conformation of the 2-thenoyl radical predict the largest hydrogen splitting to be at the position which obeys the zigzag rule, i.e., H-4 for this conformation (Wiffen, J. T. Ph.D. Thesis, 1974, University of Sussex, U.K.). The authors thank Dr. A. Hudson, Brighton, U.K., for this information.

(52) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.

MNDO Studies of the Didehydrodiazines[1]

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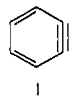
Abstract: MNDO calculations are reported for all the didehydro derivatives of pyridazine, pyrimidine, and pyrazine, and for their possible modes of rearrangement.

Like the more familiar didehydroaromatics, benzyne (**1**) and the didehydropyridines (**2** and **3**), didehydro derivatives of the three diazines (pyridazine (**4**), pyrimidine (**5**), and pyrazine (**6**)) have been postulated as intermediates in a number of reactions.[2-4] The evidence for their intervention is, however, often inconclusive, as is so often the case for reactive species postulated as intermediates in reactions, because it is usually possible to explain the formation of the observed products in other ways.

This is a situation where theoretical calculations can be very useful. While no current theoretical procedure is accurate and reliable enough to establish the existence of such a species, calculations of this kind may add productively to the body of evidence for it and may also suggest useful avenues of experimental enquiry. Indeed, MINDO/3[5] and MNDO[6] calculations for the dehydro-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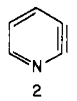

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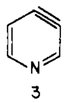

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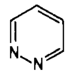

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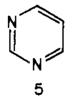

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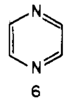

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(1) Part 67 of the series Ground States of Molecules. Part 66: Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 1744.

(2) Reinecke, M. *Tetrahedron* **1982**, 427.

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benzenes led to some surprising predictions that were subsequently proved correct by experiment.[7] Similar calculations for the dehydrodiazines seemed likely to provide equally useful information concerning their stabilities and properties. Since no theoretical calculations for didehydrodiazines seem to have been reported other than the EH study by Hoffman et al.[8] and none recently, we decided to carry out a comprehensive study of them. The method of choice in this connection was clearly MNDO[9] because it alone offers the possibility of providing adequate results for systems of this kind at reasonable cost.

Experimental Procedure

The calculations were carried out by using the standard MNDO procedure,[9,10] as implemented in the MOPAC[11] package of computer programs. Since didehydroaromatics can exhibit biradical character, the calculations were also carried out with inclusion of configuration interaction (MNDO/CI). Calculations for the corresponding triplets were carried out by using the spin-unrestricted (UHF) version (UMNDO) of MNDO, which was also used in calculations for the singlets. Reactions were followed by the reaction-coordinate method,[12] the transition states found in this way being refined by the McIver–Komornicki[13] procedure. All stationary points were characterized by calculating force constants.[13]

MNDO allows implicitly for electron correlation in normal closed-shell molecules since it contains a built-in allowance for electron correlation. In the case of a singlet biradical, where the correlation between the unpaired electrons is extreme, this allowance is inadequate, and the heats of formation calculated by MNDO for such species are correspondingly too positive. Allowance for this type of correlation must then be made explicitly by using UMNDO or MNDO/CI. In the case of normal closed-shell molecules, all three procedures give similar results, the energies calculated by them usually agreeing to <2 kcal/mol. In a "real" biradical, where the unpaired electrons are isolated from one another, the energies given by UMNDO or MNDO/CI are more negative than the MNDO ones by 40–60 kcal/mol.

Use of the UHF procedure, or inclusion of CI, compensates completely for the pair correlation between the unpaired electrons in a biradical. However, UMNDO and MNDO/CI still contain the allowance for correlation included in MNDO via the parametrization. The energies they give for biradicals are consequently too negative, by −15 kcal/mol in the case of MNDO/CI and −25 kcal/mol in the case of UMNDO.[14] The real error in the energies given by MNDO for biradicals is thus less than the difference between the UMNDO or MNDO/CI values by 15–25 kcal/mol, i.e., somewhat more than 1 eV, in the range of values found for electron-pair-correlation energies.

These comments apply only to "true" biradicals where the coupling between the unpaired electrons is negligible. In many "biradical-like" species, the unpaired electrons do interact with one another, though not enough to lead to a molecule that can be adequately represented by a classical closed-shell valence structure. In the case of such a *biradicaloid*, the difference in correlation between the "unpaired" electrons, while greater than usual, is nevertheless less than in a true biradical. The differences between the energies given by MNDO, and by UMNDO or MNDO/CI, is then correspondingly less than that for a "true" biradical, but greater than that for a "normal" molecule. Likewise the energies given by UMNDO or MNDO/CI are again too negative because of an overestimation of the correlation energy. Our experience[15] suggests that the errors are still much the same for a biradicaloid as for a true biradical, the best estimate of the heat of formation of a biradicaloid being consequently given by the MNDO/CI value *plus* 15 kcal/mol or the UMNDO value *plus* 25 kcal/mol. The difference between these values and that given by MNDO then serves as a measure of the "biradical character" of the biradicaloid. If the difference becomes negative, this indicates that the molecule is best represented as a normal closed-shell species and the MNDO values for it are accepted.

Table I. MNDO-Calculated Heats of Formation for Isomeric Diazines (kcal/mol)

compd	MNDO	UMNDO	MNDO/CI	rel heats[a]	rel EH heats[b]
7	175*	153	162	11	17
8	164*	150	155	0	0
9	177				
10		151	161*	12	19
11	209				
12		147	152*	3	21
20	165*	145	153	10	5
22	165	138	140*	0	0
23	180				
24		142	149*	9	24
28	175	141	146*	6	16
29	181	147	164*	22	26
34	179				
35		142	160*	18	22
36	167	138	142*	0	0

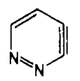
[a] Estimated relative ΔH_f's for the didehydrodiazines. The heat of formation used, either MNDO or MNDO/CI, is marked with an asterisk. As discussed in the text, 15 kcal/mol is added to MNDO/CI values. [b] Relative EH heats for the purpose of comparison (ref 8).

These rules are used in interpreting our calculations.

Results and Discussion

A. Didehydropyridazines. Because the meta and para didehydrodiazines may each have two structures, bicyclic or monocyclic, it is necessary to be able to distinguish between them. At the same time, it is also convenient to have some "generic" name which would be inclusive to both isomers. In general, a species will be named as a diazyne (for example, 3,5-pyridazyne) when we do not wish to differentiate between the two. Where appropriate, bicyclic and monocyclic isomers will be drawn and referred to by number.

Calculations were carried out for the singlet and triplet forms of all isomeric didehydro derivatives (**7**–**12**) of pyridazine (**4**). Their energies, calculated by the various procedures indicated above, are shown in Table I, and the corresponding geometries are given in Table III. As indicated above, the best estimate of the heat of formation of a diazyne is given either by the MNDO value or the MNDO/CI value plus 15 kcal/mol if this is lower than the MNDO value. The fourth column of Table I gives the relative energies of each diazyne estimated by the preceding method. The last column of the table gives the corresponding EH value.[8]



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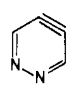

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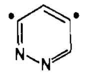

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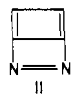

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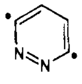

12

Of the two *o*-benzyne analogues, **7** and **8**, the latter is the more stable, by 11 kcal/mol. Both appear to have normal closed-shell structures with some biradical character, judging by the effect of CI on the energy. The geometries of **7** and **8** are indeed similar to that found previously[5,6] for *o*-benzyne itself.

The greater stability of **8** can be explained convincingly in terms of PMO theory.[16] In an AH (alternant hydrocarbon), the bond–bond polarizabilities alternate, being positive for bonds separated by an even number of carbon atoms and negative if they are separated by an odd number. In the closed-shell form of an ortho diazene, the "triple" bond is shortened and its CC π resonance integral increases correspondingly. This change in turn

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(11) QCPE Bulletin, University of Indiana, No. 455.

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(13) (a) McIver, J. W.; Komornicki, A. *Chem. Phys. Lett.*, **1971**, *10*, 303. (b) McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

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(16) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3345.

increases the bond orders of the 3,4 and 5,6 (with respect to the CC triple bond) π bonds and decreases those of the rest. In **8**, the two CN bonds thus become stronger, while the NN and the two CC bonds become weaker. A similar analysis for **7** indicates that in it the NN bond and one of the CC bonds become stronger while the CN bonds and the other CC bond become weaker. Now from Pauling's electronegativity rule, the bond energy of a bond between two dissimilar atoms, X and Y, is greater than the mean of the XX and YY bond energies. The bond energy of a C=N double bond should therefore be greater than the mean of the bond energies of a C=C bond and a N=N bond. The net effect of the change in bond length of the bond between the carbon atoms that lose hydrogen in forming the ortho didehydro derivative should therefore be more bonding, or less antibonding, in the case of **8** than **7**.

Calculations[5,6] for the benzynes indicate that the length of the bond linking the bare carbon atoms in a biradical form of the benzyne is not much greater than it is in benzene. The biradical forms of **7** and **8** should therefore have similar energies, as indeed appears to be the case (Table I). Forming the "triple" bond leads to a decrease in the correlation energy between the two initially unpaired electrons but also to a gain in bonding energy, due to the formation of an extra bond. The change in correlation energy should again be the same for both isomers since it corresponds to the formation of a bent but localized π bond. Formation of this bond also, however, leads to a decrease in the corresponding CC bond length and hence to a change in the energy of the delocalized π electrons, which, as we have seen, is more favorable in the case of **8** than **7**. In the case of **8**, formation of the extra CC bond becomes even more favorable than in the case of *o*-benzyne, so **8** has even less biradical character than *o*-benzyne does. In **7**, however, the net change in the energy of the π electrons is positive and nearly sufficient to outweigh the formation of the extra CC bond. **7**, consequently, is expected to have a greater biradical character than **8**.

While there seems little doubt that substituted derivatives of **8** have been formed as transient intermediates in several reactions,[17-20] no evidence has yet been presented for the existence of **7**. Its radical cation ($7^{+\cdot}$) does, however, seem to be formed as an intermediate in the decomposition of pyridazine-3,4-dicarboxylic anhydride (**13**) by electron impact.[21] The corresponding mass spectrum showed a strong peak at *m/e* 78. Similar treatment of the isomeric anhydride (**14**) led to a mass spectrum with a weak peak at *m/e* 78, together with a strong one at *m/e* 50, suggesting that $14^{+\cdot}$ loses carbon monoxide and carbon dioxide to form $8^{+\cdot}$ (*m/e* 78) but that this rapidly loses nitrogen to form the radical cation derived from diacetylene (**15**) (*m/e* 50). Benzene also gives rise to a species with *m/e* 50 under the same conditions, presumably by loss of acetylene from its radical cation, but the corresponding peak in the mass spectrum of benzene is weak. This difference can of course be attributed to the well-known tendency for N_2 to be eliminated from compounds containing nitrogen atoms linked together, due to the great strength of the N≡N bond. Pyrolysis of the triazine (**16**) also leads to loss of nitrogen presumably from the intermediate aryne (**17**) leading to diphenyldiacetylene (**18**).[17]

We studied the decomposition of **8** using MNDO, MNDO/CI, and UMNDO. Stationary points corresponding to transition states (TS) were found without difficulty in all three cases and were characterized as such by calculating force constants.[13] All three transition states were essentially identical and had virtually identical heats of formation (MNDO, 192 kcal/mol; UMNDO, 191 kcal/mol). The TS is thus a normal closed-shell species with no biradical character. Figure 1 shows the MNDO geometry. The barrier to dissociation is 28 kcal/mol, implying that **8** should be reasonably stable, even at elevated temperatures. Note that the TS is unsymmetrical, implying that elimination of nitrogen from **8** is not synchronous. This would be expected on the basis of a recently formulated rule[22] because the conversion of **8** to nitrogen and **15** is a two-bond process.

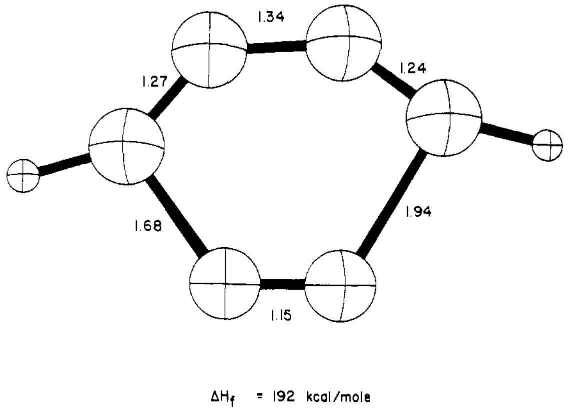

Figure 1.

The only *m*-benzyne analogue derivable from pyridazine is its 3,5-didehydro derivative which might exist (Cf. ref 6) either as a closed-shell species, 2,3-diazabicyclo[3.1.0]hexatriene (**9**), or as a monocyclic biradicaloid (**10**). Since MNDO underestimates the stabilities of biradicals, it is not surprising that it predicts **9** to be the only minimum on the corresponding potential surface. The transannular bond (C_1C_5) in **9** is predicted to be long (1.60 Å), as expected,[6] and its calculated heat of formation, while appreciably greater than that of **8**, is only a little greater than that of **7**.

UMNDO and MNDO/CI, on the other hand, both overestimate the stabilities of biradicals. It is therefore equally understandable that both procedures predict the biradicaloid (**10**) to be the only stable form of the 3,5-isomer. The heats of formation calculated for **10**, when corrected as indicated above, are, however, almost the same as the MNDO value for **9**. Both isomers are therefore probably comparable in energy and both may well correspond to minima on the potential surface. Similar isomerism has been predicted[6] by MNDO in the case of *m*-benzyne. Since evidence has been presented (see ref 5) for the existence of both **8** and *m*-benzyne as reaction intermediates, it seems likely that 3,5-pyridazyne should also be obtainable. It may indeed be chemically more stable than **8**, given that it cannot form a normal closed-shell molecule by loss of nitrogen. As yet no evidence for its existence has been reported.

Table I shows the heats of formation calculated for **9** and **10** and Table III the corresponding geometries.

Similar results followed for the unique *p*-benzyne analogue. MNDO predicted this also to have a closed-shell ground state, corresponding to 2,3-diazabicyclo[2.2.0]hexatriene (**11**) while both MNDO/CI and UMNDO favored a monocyclic biradical structure (**12**). Here, however, the classical structure (**11**) was predicted to be very much higher in energy than **7** or **8** (Table I). The differences in energy between it and those predicted for **11** by MNDO/CI (57 kcal/mol) or UMNDO (62 kcal/mol) were moreover very large, implying that **12** is close to being a true biradical and that **11** very probably does not correspond to a minimum on the potential surface. Here again no evidence has been reported for the stable existence of either species.

While **12**, like 3,5-pyridazyne, cannot form a normal molecule by loss of nitrogen, it can, unlike the 3,5-isomer, undergo electrocyclic ring opening to form maleonitrile (**19**). Since the ease

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(17) Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. *Chem. Commun.* **1973**, 819.

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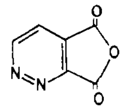
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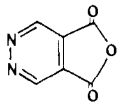
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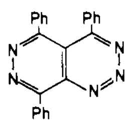
$[\text{H-C}\equiv\text{C-C}\equiv\text{C-H}]^{+\cdot}$

15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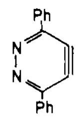
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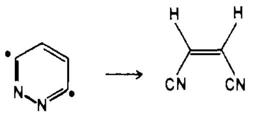
$\text{Ph-C}\equiv\text{C-C}\equiv\text{C-Ph}$

18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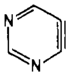
of such a reaction cannot be estimated from analogy or any kind of qualitative treatment or chemical intuition and since the ability of **12** to exist as an (matrix) isolable species probably depends on it, we decided to study its conversion to **19** using MNDO. Since **12** rather than **11** is evidently the ground state, it was clearly necessary to use either MNDO/CI or UMNDO to study its decomposition. We chose the latter because use of MNDO/CI in such connections is expensive, due to technical problems in calculating geometries.[23]

No problems arose in studying the conversion. Figure 2 shows the geometry and heat of formation calculated for the transition state. The corresponding activation energy is very small (14 kcal/mol), suggesting that attempts to prepare **12** (**11**) will need to be carried out at low temperatures.

B. Didehydropyrimidines. Table I shows the heats of formation calculated for the closed-shell and biradical forms of the only *o*-benzyne analogue from pyrimidine, i.e., 4,5-pyrimidyne (**20**), which again appears to be a classical molecule, the differences between the energies calculated for it by MNDO and by MNDO/CI or UMNDO (12 and 20 kcal/mol, respectively) being less than the critical values indicated above. The MNDO geometry, which corresponds nicely to that expected for a 1,2-aryne, is included in Table III.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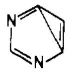
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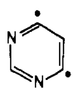
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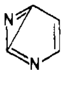
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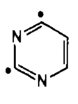
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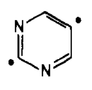
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The existence of **20** as a reaction intermediate seems to have been established[2-4] by studies of the reactions of 6-halo derivatives of deuteriated 4-*tert*-butyl- and 4-phenylpyrimidines with base,[24-26] by the suppression of cine substitution by proton donors,[4,27,28] and (most conclusively) by trapping the aryne intermediates by Diels–Alder reactions with furan.[29]

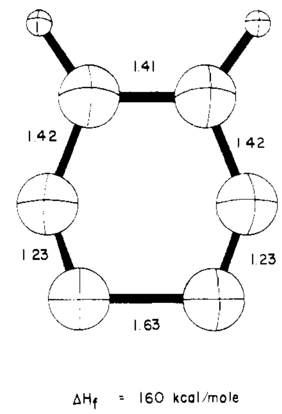

Figure 2.

Table II. MNDO-Calculated Heats of Formation for **25–27** (kcal/mol)

compd	MNDO
25	113
26	198
27	178

Table III. Bond Lengths of Didehydrodiazines (in Angstroms)

compd	method	1–2	2–3	3–4	4–5	5–6	6–1	trans-annular
7	MNDO	1.30	1.34	1.26	1.37	1.45	1.38	
	UMNDO	1.29	1.34	1.35	1.38	1.44	1.38	
	MNDO/CI	1.30	1.34	1.30	1.37	1.44	1.37	
8	MNDO	1.26	1.40	1.37	1.27	1.37	1.40	
	UMNDO	1.27	1.40	1.39	1.33	1.39	1.40	
	MNDO/CI	1.27	1.40	1.39	1.33	1.39	1.40	
9	MNDO	1.30	1.35	1.38	1.38	1.39	1.39	1.58
10	UMNDO	1.29	1.34	1.40	1.39	1.39	1.39	
	MNDO/CI	1.30	1.31	1.40	1.36	1.39	1.37	
11	MNDO	1.32	1.38	1.39	1.47	1.39	1.38	1.58
12	UMNDO	1.32	1.32	1.40	1.43	1.40	1.32	
	MNDO/CI	1.37	1.28	1.40	1.41	1.40	1.28	
20	MNDO	1.36	1.40	1.31	1.27	1.38	1.37	
	UMNDO	1.36	1.39	1.32	1.35	1.39	1.37	
	MNDO/CI	1.36	1.39	1.32	1.30	1.38	1.37	
22	MNDO	1.38	1.38	1.29	1.39	1.39	1.29	2.12
	UMNDO	1.37	1.38	1.31	1.39	1.39	1.30	
	MNDO/CI	1.37	1.37	1.31		1.39	1.31	
23	MNDO	1.31	1.36	1.34	1.38	1.43	1.40	1.67
24	UMNDO	1.33	1.34	1.32	1.39	1.43	1.37	
	MNDO/CI	1.31	1.35	1.32	1.39	1.41	1.37	
28	MNDO	1.30	1.26	1.48	1.32	1.36	1.40	
	UMNDO	1.33	1.33	1.38	1.39	1.39	1.38	
	MNDO/CI	1.31	1.31	1.39	1.37	1.37	1.39	
29	MNDO	1.25	1.66	1.25	1.39	1.39	1.39	
	UMNDO	1.32	1.37	1.32	1.38	1.43	1.38	
	MNDO/CI	1.32	1.32	1.32	1.38	1.43	1.38	
34	MNDO	1.38	1.39	1.35	1.35	1.39	1.38	
35	UMNDO	1.33	1.40	1.36	1.37	1.40	1.33	
	MNDO/CI	1.33	1.39	1.36	1.37	1.39	1.33	
36	MNDO	1.27	1.37	1.41	1.27	1.37	1.41	
	UMNDO	1.31	1.40	1.39	1.31	1.40	1.38	
	MNDO/CI	1.29	1.38	1.39	1.29	1.38	1.39	

Two analogues, 4,6-pyrimidyne and 2,4-pyrimidyne, of *m*-benzyne can in principle exist in the pyrimidine series.

Unlike other meta diazynes, the bicyclic form of the 4,6-isomer (**21**) was not predicted to be a minimum by MNDO, the transannular distance between positions 4 and 6 being 2.12 Å. Interactions between the singly occupied lobes and the adjacent nitrogen pairs likely account for the monocyclic structure. MNDO/CI and UMNDO, as usual, also favor the monocyclic form (**22**). Since the differences in energy between the values calculated by MNDO and by MNDO/CI or UMNDO for **22**

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(23) Inclusion of CI leads to bond order matrices which are not variationally optimized. This greatly increases the computing time needed for the calculation of derivatives of the energy with respect to the geometrical variables.

(24) van der Plas, H. C.; Smit, P.; Koudijs, A. *Tetrahedron Lett.* **1968**, 9. A referee has pointed out that a mechanism other than elimination addition has been advanced for the reaction of 6-bromo-4-*tert*-butylpyrimidine with base (Rasmussen, C. A. H.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 5). The evidence for the existence of 4,5-pyrimidyne, in the authors opinion, remains strong.

(25) de Valk, J.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 1239.

(26) van der Plas, H. C. *Acc. Chem. Res.* **1978**, *11*, 462.

(27) Kauffmann, T.; Nurnberg, R.; Udluft, K. *Chem. Ber.* **1969**, *102*, 1177.

(28) Kauffmann, T.; Nurnberg, R.; Udluft, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 617.

(29) Christophe, D.; Promel, R.; Maeck, M. *Tetrahedron Lett.* **1978**, 4435.

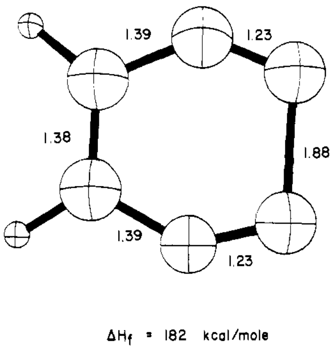
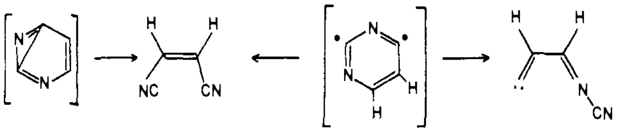


Figure 3.

are large (MNDO/CI, 25 kcal/mol; UMNDO, 27 kcal/mol), 4,6-pyrimidyne is probably a biradical. MNDO/CI predicts **22** to be the most stable of the pyrimidynes (Table I). Its geometry is given in Table III.

The other *m*-benzyne analogue was, however, predicted by MNDO not to exist as a stable species. A stationary point was located on the MNDO potential surface, corresponding to the bicyclic form (**23**), but calculation of its force constants showed it to be a saddle point, i.e., a transition state, not a minimum. We were able to show without difficulty that **23** is converted without activation to *cis*-1-cyanovinyl isocyanide (**25**), so it is clearly the transition state for rearrangement of **25** to something else. Our efforts to find what this something is were, however, unsuccessful. We also found a second saddle point (**26**) which proved to be the transition state for interconversion of **25** and the isomeric carbene (**27**).

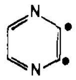


23 25 26 27

UMNDO and MNDO/CI did, however, predict the monocyclic species (**24**) to be a minimum on the potential surface. If 2,4-pyrimidine exists at all, it is therefore a biradical. Heats of formation for **23–27** are found in Tables I and II and corresponding geometries for **23** and **24** are in Table III.

Calculations for the sole *p*-benzyne analogue from pyrimidine, i.e., 2,5-pyrimidyne (**28**), indicate it to be also biradical-like. Inclusion of CI lowers it's energy by 30 kcal/mol (Table I). The geometry calculated for it by MNDO/CI is shown in Table III.

As yet there is no definite evidence for the existence of any of these *m*- and *p*-benzyne analogues. Reactions leading to products which might have been formed by aryne mechanisms have been shown to involve instead either ANRORC[25,26] ring openings[30–34] or addition–elimination mechanisms.[32,34,35] However, none seem as yet to have tried using bases other than alkali metal amides, which are of course powerful nucleophiles.



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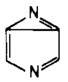

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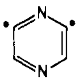

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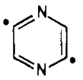

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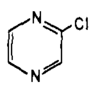
C. Didehydropyrazines. 2,3-Pyrazyne (**29**) differed from the other *o*-benzyne analogues in that the energy calculated for it by MNDO/CI (Table I) was significantly lower (by 17 kcal/mol) than that given by MNDO (Table I). **29** is therefore best represented by the indicated biradical structure. The geometry calculated for it by MNDO/CI is shown in Table III.

No clear evidence has yet been found for the existence of **29**. Lont et al.[36] have shown that the amination of 2-chloropyrazine (**30**) with potassium amide takes place exclusively by a ring-opening (ANRORC[25,26]) mechanism. However, pyrolysis of pyrazine-2,3-dicarboxylic anhydride (**31**) in benzene gave a small amount of 2-phenylpyrazine (**32**), whose formation could be represented as a radical attack at benzene by the biradical (**29**),[37] and pyrolysis in the absence of benzene gave maleonitrile (**19**), which could well have been formed by ring opening of **29** to form 1,2-diisocyanatoethylene (**33**) followed by a double isocyanide–cyanide rearrangement.[38]



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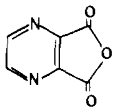

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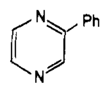

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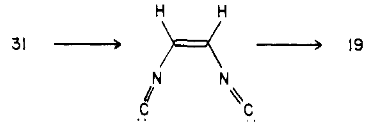

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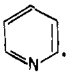
Further calculations showed that while **29** correspondings to a minimum on the MNDO potential surface, the barrier to rearrangement to **33** is only 1 kcal/mol. The TS for the same rearrangement on the UMNDO potential surface proved to be identical with the MNDO one (Figure 3), indicating the absence of biradical character. Applying the usual correction of 15 kcal/mol to the MNDO/CI heat of formation for **29** (see above), we arrive at a final estimate of 3 kcal/mol for the activation energy for **29** to **33**. These results support the postulated[38] formation of **29** as an intermediate in the pyrolysis of **31**.

In the case of the *m*-benzyne and *p*-benzyne analogues, 2,6-pyrazyne and 2,5-pyrazyne, MNDO/CI gives energies that are more negative than the MNDO ones by 19 and 25 kcal/mol, respectively. As was the case with the other 1,3-diazynes (except 4,6-pyrimidyne), MNDO predicted a closed-shell bicyclic structure (**34**) whereas UMNDO and MNDO/CI predicted a monocyclic biradicaloid (**35**). Since the difference between the MNDO and (corrected) MNDO/CI heats of formation is small, both in fact may be stable species. On the other hand, both MNDO and MNDO/CI predict only the monocyclic structure (**36**) in the case of the para isomer probably because of stabilizing interactions between the singly occupied AOs of the "radical" centers and the adjacent nitrogen lone pairs. This view is supported by the results of Bower et al.[39] in which the ESR spectra of γ-irradiated pyridine (**2**) was interpeted as being that of 2-pyridyl radical (**37**) rather than the expected $\mathbf{2}^{+\cdot}$



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The heats of formation calculated for **34–36** are shown in Tables I and the corresponding geometries in Table III. No evidence for the existence of either species has as yet been reported.

Conclusions

The work reported here suggests that the didehydrodiazines should generally resemble the benzynes but with some interesting

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(30) van Meeteren, H. W.; van der Plas, H. C. *Tetrahedron Lett.* **1966**, 4517.

(31) van Meeteren, H. W.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 105.

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(37) Fields, E. K.; Meyerson, S. *J. Org. Chem.* **1966**, *31*, 3307.

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(39) Bower, H. J.; McRae, J. A.; Symons, M. C. R. *Chem. Commun.* **1967**, 542.

differences. For example, it seems surprising at first sight that the two *ortho* pyridazynes are predicted to differ so much in energy. The difference can, however, be explained at once in terms of PMO theory. Several of the didehydrodiazines are also predicted to undergo ring opening or loss of nitrogen relatively easily, unlike their benzyne analogues. This difference can again be easily explained, being due to the fact that the C≡N and N≡N triple bonds are much stronger than C≡C. Perhaps the most interesting conclusion is that several of the meta and para didehydrodiazines should, like *m*- and *p*-benzyne, be relatively stable species. As yet there is not evidence for the intervention of 1,3- or 1,4-didehydro derivatives of aromatic compounds as reaction intermediates; yet our calcultions suggest that they should often be comparable in stability with their 1,2 counterparts.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. F49620-83-C-0024) and the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out on a DEC VAX 11-780 computer purchased with funds provided by the National Science Foundation (Grant CHE78-03213) and the University of Texas at Austin.

Registry No. **7**, 83421-60-7; **8**, 83421-61-8; **9**, 91202-21-0; **10**, 91202-22-1; **11**, 91202-23-2; **12**, 91202-24-3; **20**, 20722-78-5; **22**, 91202-25-4; **23**, 91202-26-5; **24**, 91202-27-6; **25**, 91202-28-7; **27**, 91202-29-8; **28**, 91202-30-1; **29**, 91202-31-2; **34**, 91202-32-3; **35**, 91202-33-4; **36**, 91202-34-5.

On the Structure of *tert*-Butyl Hypoiodite

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada. *Received November 2, 1983*

Abstract: A compound known as "*tert*-butyl hypoiodite" has hitherto been referred to in the literature as a reagent with some synthetic utility. Three methods of preparation have been used to make this material: the reaction of *tert*-butyl hypochlorite with iodine, the reaction of *tert*-butyl hypochlorite with metal iodides, and the reaction of potassium *tert*-butoxide with iodine. Physical and chemical evidence is offered to show that the reagent obtained from the first of these methods is different from that made from the latter two methods. Reaction schemes are proposed to account for the different properties and reactivities of the two reagents. Structures are proposed for the two reagents which rationalize both the physical and chemical properties of the two materials.

In recent years organic hypoidodites, generated in situ, have found a considerable use in organic synthesis. In particular a reagent which can be formally considered to be "*tert*-butyl hypoiodite" has been used to good effect both as a homolytic and heterocyclic source of iodine. Although its use is well documented, to date no convincing physical evidence has been presented regarding the structure of this compound.

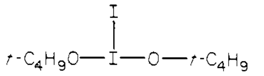
Walling[5] in his studies of the free-radical chlorination reactions of *tert*-butyl hypochlorite observed that iodine, normally a free-radical scavenger, accelerated the reaction. It was evident that *tert*-butyl hypochlorite reacted with iodine to produce a species that reacts faster than *tert*-butyl hypochlorite itself.

Organic hypoiodites first found a synthetic use in steroid chemistry. Barton[6] used "*tert*-butyl hypoiodite" as a reagent to prepare steroid hypoiodites from steroidal alcohols. These were used as intermediates in an intramolecular hydrogen abstraction reaction; i.e., they were photolyzed and underwent a 1,5-carbon to oxygen hydrogen abstraction, followed by iodination and subsequent ring closure of the iodo alcohols. The "*tert*-butyl hypoiodite" was generated by the reaction of potassium *tert*-butoxide with iodine or the reaction of *tert*-butyl hypochlorite and iodine. Barton proposed that the second reaction produced a mixture of *tert*-butyl hypoiodite and iodine monochloride. Similar steroid reactions were extensively studied by Heusler.[7] The "steroid hypoiodites" were generated by using lead tetraacetate and iodine, presumably via the intermediacy of acetyl hypoiodite.

Barton[8] used "*tert*-butyl hypoiodite" to prepare *N*-iodoamides. On photolysis the compounds underwent an intramolecular hydrogen abstraction to give imino lactones which were hydrolyzed to lactones. Again the "*tert*-butyl hypoiodite" was formed from the reaction of *tert*-butoxide or *tert*-butyl hypochlorite with iodine.

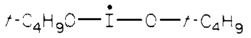
Barton[9] again used "*tert*-butyl hypoiodite" in a "Hunsdieker" type reaction to decarboxylate carboxylic acids. He reported good yields of iodocyclohexane from cyclohexanecarboxylic acid and showed this to be a useful way to synthesize bridgehead iodides.[9,11] Goosen[10] studied this reaction with a range of para substituted phenylacetic acids. He concluded that an acyl hypoiodite was an intermediate and reported a ρ value of -1.09 for its decomposition.

In this laboratory "*tert*-butyl hypoiodite" was generated from *tert*-butyl hypochlorite and mercuric iodide[12] and was used in the free-radical iodination of alkanes. The reaction represented a unique way to carry out this transformation. The substitution proceeded in good yield and with a high selectivity (k_s/k_p = 29:1).[12] On the basis of the high selectivity it was postulated that the "*tert*-butyl hypoiodite" exists as a 10-I-3 hypervalent species, **1**, and that the hydrogen abstracting species was an 9-I-2 iodonyl radical, **2**.



$t\text{-}C_4H_9O-\overset{\overset{I}{|}}{I}-O-t\text{-}C_4H_9$

1



$t\text{-}C_4H_9O-\dot{I}-O-t\text{-}C_4H_9$

2

These conclusions are in good accord with similar work that has been done on the selectivity exhibited by an iodonyl radical in this[13-15] and other[16,17] laboratories. Iodine(III) radical species

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(1) Postdoctoral Fellow, University of Alberta, 1966-68.

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(3) Taken in part from: J. E. Rowe, Ph.D. Thesis, University of Alberta, 1974.

(4) Postdoctoral Fellow, University of Alberta, 1982-83.

(5) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108.

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