The gap between 11.7 and 13.6 eV on the calculated energy scale is visible on the spectra between 12.0 and 12.5 eV. Then the $\pi 2b_1$ and $1a_2$ MO's arise, followed by the σ_{C-N} and σ_{C-C} orbitals. The differences between the two spectra around 13.7 eV are due to the presence of additional σ_{C-C} and σ_{C-H} orbitals in the dimethylated compound.

Concluding Remarks

Theoretical ab initio calculations shed some light on the molecular structure of 3,5,11,13-tetraazacycl[3.3.3]azine: the Mulliken population analysis indicates a nonnegligible involvement of the central nitrogen lone pair in the delocalization pattern. XPS results on C1s and N1s core levels confirm this assumption, the central nitrogen appearing much less negative than the others. The UV PES spectra may be successfully interpreted on the basis of Koopmans' theorem and correlated with the calculated molecular orbital energies.

The usefulness of the joint study of the theoretical and XPS, UV PES experimental results is thus firmly established in the field on aromatic nitrogen-containing compounds.

Acknowledgment. Helpful discussions with Dr J. Riga (Namur) and Drs. D. Gonbeau and C. Guimon (Pau) are greatly acknowledged. We thank F. Gracian (Pau) and Ph. Henrot (Namur) for technical assistance. One of us (J.P.B.) is grateful to the F.N.R.S. (Belgium) and to the Belgian–French exchange program with the C.N.R.S (France) for assistance during his stay at the University of Pau.

Registry No. I, 38713-73-4; **II**, 38713-72-3.

Semiempirical Calculation of Diamagnetic Susceptibilities of Alkyl β-Aminovinyl Ketones

R. R. Gupta,* Ratan Swaroop, M. Kumar, and Kishan

Contribution from the Department of Chemistry, University of Rajasthan, Jaipur-302004, India.

Received January 11, 1984

Abstract: Diamagnetic susceptibilities of alkyl β-aminovinyl ketones have been calculated theoretically by different theoretical approaches. The wave-mechanical approach, however, gives due consideration to the contributions of all types of electrons, but still the agreement between experimental and theoretical values is not satisfactory. The semiempirical approach, in which diamagnetic susceptibility is considered to be contributed by atoms, bonds, and bond–bond interactions, provided excellent results of diamagnetic susceptibility irrespective of the existing different structural environments. The divergency between experimental and theoretical values of diamagnetic susceptibility is less than 1%. Such an excellent agreement is due to the fact that all the existing structural factors have been duly accounted for in the form of parameters.

Diamagnetic susceptibility has been fascinating to the scientists since it has proved its unique importance by giving structural information on resolving various existing structural controversies in structural chemistry. But the diamagnetic studies, in view of their relationship with the structure, require theoretical estimations of diamagnetic susceptibilities for analyzing different existing structural environments, since such structural environments affect considerably the molecular diamagnetism. Although a number of methods,[1-5] based on either the atomic susceptibility concept or the bond susceptibility concept, have been developed to calculate diamagnetic susceptibilities of organic compounds but could not provide satisfactory results of diamagnetic susceptibility even for simple organic compounds. It is, therefore, considered interesting to develop a semiempirical approach to calculate diamagnetic susceptibilities of the alkyl β-aminovinyl ketones analogous to that reported for the simple organic and organometallic compounds,[6-8] since alkyl β-aminovinyl ketones form an interesting and exciting series of organic compounds, from a structural point of view, because of the presence of a carbonyl group in conjugation with doubly bonded carbon atom and due to the presence of a nitrogen atom having a lone pair of electrons. The results obtained by theoretical approaches, other than the semiempirical approach, have also been analyzed in the light of structural factors prevailing in the alkyl β-aminovinyl ketones and contributing considerably to the molecular diamagnetism.

Diamagnetic susceptibilities of the alkyl β-aminovinyl ketones have been calculated theoretically by the Pascal, Pacault, and Hoarau method, based on the atomic susceptibility concept, and the wave–mechanical method, based on the bond susceptibility concept, in order to analyze different existing structural environments and to correlate these structural environments with the theoretical results. The Pascal, Pacault, and Hoarau method considers the contributions of atoms and the correction factors of the methyl group. The wave–mechanical approach has been applied to calculate diamagnetic susceptibilities by using the contributions of (i) inner-shell electrons of each atom present, (ii) bonding electrons in each bond, (iii) a nonbonding lone pair of electrons present in the outer shell, and (iv) π-electrons in the form of the following expression:

$$\chi_M = \sum\chi_{ISE} + \sum\chi_{BE} + \sum\chi_{NBE} + \sum\chi_{\pi\text{-electrons}}$$

The results of diamagnetic susceptibility of the alkyl β-aminovinyl ketones, obtained by the Pascal, Pacault, and Hoarau method as well as the wave–mechanical approach, are summarized in Table I.

A critical examination of the theoretical results of diamagnetic susceptibility of the alkyl β-aminovinyl ketones, calculated by the

---

(1) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5.

(2) Yang, Y. *J. Chem. Phys.* **1948**, *16*, 865.

(3) Pascal, P.; Gallais, F.; Labarre, J. F. *C. R. Hebd. Seances Acad. Sci.* **1951**, *252*, 2624.

(4) Pascal, P.; Pacault, A.; Hoarau, J. *C. R. Hebd. Seances Acad. Sci.* **1951**, *233*, 1078.

(5) (a) Baudet, J.; Tillieu, J.; Guy, J. *C. R. Hebd. Seances Acad. Sci.* **1957**, *244*, 2920. (b) Baudet, J. *J. Chim. Phys.* **1961**, *58*, 228. (c) Baudet, J.; Guy, J.; Tillieu, J. *J. Phys. Radium* **1960**, *21*, 600.

(6) (a) Hameka, H. F. *J. Chem. Phys.* **1961**, *34*, 1996. (b) O'Sullivan, P. S.; Hameka, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 25; 1821.

(7) Burnham, A. K.; Lee, J.; Schmalz, T. G.; Beak, P.; Flygare, W. H. *J. Am. Chem. Soc.* **1977**, *99*, 1836.

(8) (a) Mital, R. L.; Gupta, R. R. *J. Am. Chem. Soc.* **1969**, *91*, 4664. (b) Gupta, R. R.; Kumar, M.; Ojha, K. G. *J. Chem. Phys.* **1981**, *75*, 4173; **1982**, *76*, 1173; 5182. (c) Gupta, R. R.; Kumar, M. *Chem. Phys. Lett.* **1983**, *100*, 297.

0002-7863/84/1506-4378$01.50/0

Table I. Diamagnetic Susceptibilities of Alkyl β-Aminovinyl Ketones

compound	formula	parameters	χ_M-(exptl)[a]	Pascal Pacault, & Hoarau method	χ_M-(theor), wave-mechanical method	semi-empirical method
methyl β-aminovinyl ketone	$CH_3C({=}O)CH{=}CHNH_2$	$A + D$	44.23	46.83	53.29	43.68
ethyl β-aminovinyl ketone	$C_2H_5C({=}O)CH{=}CHNH_2$	$A + B + D$	55.58	58.19	64.64	55.14
n-propyl β-aminovinyl ketone	$C_3H_7C({=}O)CH{=}CHNH_2$	$A + 2B + D$	67.01	69.55	75.99	66.60
isopropyl β-aminovinyl ketone	$i\text{-}C_3H_7C({=}O)CH{=}CHNH_2$	$A + 2B + C + D$	67.99	70.40	75.99	67.64
isobutyl β-aminovinyl ketone	$i\text{-}C_4H_9C({=}O)CH{=}CHNH_2$	$A + 3B + C + D$	79.38	81.76	87.34	79.10
methyl β-(ethylamino)vinyl ketone	$CH_3C({=}O)CH{=}CHNHC_2H_5$	$A + 2B + E$	65.41	70.40	76.46	65.56
n-propyl β-(ethylamino)vinyl ketone	$C_3H_7C({=}O)CH{=}CHNHC_2H_5$	$A + 4B + E$	88.47	93.12	99.16	88.48
n-butyl β-(ethylamino)vinyl ketone	$C_4H_9C({=}O)CH{=}CHNHC_2H_5$	$A + 5B + E$	100.02	104.48	110.51	99.54
methyl β-(dimethylamino)vinyl ketone	$CH_3C({=}O)CH{=}CHN(CH_3)_2$	$A + 2B + 2E - D + F$	67.61	71.25	76.93	67.52
ethyl β-(dimethylamino)vinyl ketone	$C_2H_5C({=}O)CH{=}CHN(CH_3)_2$	$A + 3B + 2E - D + F$	79.03	80.91	88.28	78.98
n-propyl β-(dimethylamino)vinyl ketone	$C_3H_7C({=}O)CH{=}CHN(CH_3)_2$	$A + 4B + 2E - D + F$	90.81	92.27	99.62	90.44
isobutyl β-(dimethylamino)vinyl ketone	$i\text{-}C_4H_9C({=}O)CH{=}CHN(CH_3)_2$	$A + 5B + C + 2E - D + F$	103.02	104.48	110.98	102.94
methyl β-(diethylamino)vinyl ketone	$CH_3C({=}O)CH{=}CHN(C_2H_5)_2$	$A + 4B + 2E - D + F$	90.17	92.27	99.63	90.44

[a] Gupta, R. R. "Diamagnetic Susceptibilities and Anisotropies in Landoldt Bornstein Series"; Springer-Verlag: Berlin, in press.

Pascal, Pacault, and Hoarau method, reveals that the theoretical values of diamagnetic susceptibility deviate very much from their experimental values. The wave–mechanical approach too, in which although the contributions of all types of electrons have been duly accounted for, could not provide satisfactory results of diamagnetic susceptibility for the alkyl β-aminovinyl ketones, and they differ considerably from their corresponding experimental values of diamagnetic susceptibility. Such a high order of discrepancies in the Pascal, Pacault, and Hoarau method as well as in the wave–mechanical approach is probably because of the ignorance of the environmental conditions present in the alkyl β-aminovinyl ketones due to the presence of a carbonyl group in conjugation with doubly bonded carbon atom and a nitrogen atom with a lone pair of electrons, which result in conjugation and change of the hybridization of the orbital of unshared electrons and affect considerably the molecular diamagnetism in addition to the other structural factors.

Therefore, the Pascal, Pacault, and Hoarau method, based on the atomic susceptibility concept, as well as the even wave–mechanical approach, based on the bond susceptibility concept, cannot be applied satisfactorily to calculate diamagnetic susceptibilities of the alkyl β-aminovinyl ketones because they do not consider all the structural environments persisting in these molecules and contributing considerably to the molecular diamagnetism.

Since none of the methods could provide satisfactory results of diamagnetic susceptibility for the alkyl β-aminovinyl ketones, a semiempirical appraoch has been developed to calculate diamagnetic susceptibilities of the alkyl β-aminovinyl ketones in the light of different existing structural factors with a hope of obtaining interesting results of diamagnetic susceptibility.

In the semiempirical approach, diamagnetic susceptibility has been considered to be contributed by the bond–bond interactions between two adjacent bonds in addition to the contributions of atoms and bonds and can be expressed by eq 1.

$$\chi_{\mathrm{M}} = \sum \chi_{\mathrm{atoms}} + \sum \chi_{\mathrm{bonds}} + \sum \chi_{\mathrm{bond-bond\ interactions}} \qquad (1)$$

The diamagnetic susceptibility expression for alkyl β-aminovinyl ketones having general formula $C_nH_{2n+1}C(=O)CH=CHNR_2$ (where R may be hydrogen atom or alkyl group) can be expressed as

$$\begin{aligned}\chi_{\mathrm{M}} = {} & (2n + 1)\chi_{\mathrm{C}} + \chi_{\mathrm{O}} + \chi_{\mathrm{N}} + \chi_{\mathrm{CO}} + n\chi_{\mathrm{CC}} + \chi_{\mathrm{C{=}C}} + \\ & [(2n + 1) + 2]\chi_{\mathrm{CH}} + \chi_{\mathrm{CN}} + 2\chi_{\mathrm{NR}} - \chi_{\mathrm{C{=}C:CN}} - 2\chi_{\mathrm{CO:CC}} - \\ & \chi_{\mathrm{C{=}C:CC}} - n\chi_{\mathrm{CC:CC}} - (4n - 1)\chi_{\mathrm{CO:CH}} - \\ & [2(n + 1) - 2]\chi_{\mathrm{CH:CH}} - 2\chi_{\mathrm{CN:NR}} + 2\chi_{\mathrm{R}}\end{aligned}$$

Table II. Values of Parameters

parameter	value	parameter	value
A	17.08	*D*	26.60
B	11.46	*E*	25.56
C	1.04	*F*	3.004

where the terms χ_{C}, χ_{O}, and χ_{N} are the susceptibility contributions that account for the carbon, oxygen, and nitrogen atoms. χ_{CC}, χ_{CO}, χ_{CN}, χ_{NR}, $\chi_{\mathrm{C{=}C}}$, and χ_{CH} stand for the susceptibility contributions of electron pairs in C=C, C=O, C—N, N—R, C=C, and C—H bonds. $\chi_{\mathrm{C{=}C:CN}}$, $\chi_{\mathrm{CO:CC}}$, $\chi_{\mathrm{C{=}C:CC}}$, $\chi_{\mathrm{CC:CC}}$, $\chi_{\mathrm{CO:CH}}$, $\chi_{\mathrm{CH:CH}}$, and $\chi_{\mathrm{CN:NR}}$ are the susceptibility contributions for bond–bond interactions.

Since various parameters have been used in a specific combination to account for all the structural factors contributing to the molecular dimagnetism, they have been reduced to the following parameters for simplifying the semiempirical calculations:

$$A = \chi_{\mathrm{C}} + 4\chi_{\mathrm{CH}} + \chi_{\mathrm{CC}} - 2\chi_{\mathrm{CC:CH}} - 5\chi_{\mathrm{CH:CH}}$$

$$B = \chi_{\mathrm{C}} + \chi_{\mathrm{CC}} + 2\chi_{\mathrm{CH}} - \chi_{\mathrm{CC:CC}} - 4\chi_{\mathrm{CC:CH}} - \chi_{\mathrm{CH:CH}}$$

$$C = 2\chi_{\mathrm{CC:CH}} - \chi_{\mathrm{CC:CC}} - \chi_{\mathrm{CH:CH}}$$

$$\begin{aligned}D = {} & 3\chi_{\mathrm{C}} + \chi_{\mathrm{O}} + \chi_{\mathrm{N}} + \chi_{\mathrm{CO}} + \chi_{\mathrm{C{=}C}} + \chi_{\mathrm{CC}} + 2\chi_{\mathrm{CH}} + \\ & \chi_{\mathrm{CN}} + 2\chi_{\mathrm{NH}} - \chi_{\mathrm{C{=}C:CN}} - 2\chi_{\mathrm{CN:NH}} - \chi_{\mathrm{CH:CN}} - \\ & 2\chi_{\mathrm{C{=}C:CH}} - \chi_{\mathrm{CC:CH}} - 2\chi_{\mathrm{CO:CC}} + 2\chi_{\mathrm{CH:CH}}\end{aligned}$$

$$\begin{aligned}E = {} & 5\chi_{\mathrm{C}} + \chi_{\mathrm{O}} + \chi_{\mathrm{N}} + \chi_{\mathrm{CO}} + 7\chi_{\mathrm{CH}} + \chi_{\mathrm{C{=}C}} + \\ & 2\chi_{\mathrm{CC}} + 2\chi_{\mathrm{CN}} + \chi_{\mathrm{NH}} - 2\chi_{\mathrm{CC:CO}} - \chi_{\mathrm{CC:CH}} - \chi_{\mathrm{C{=}C:CH}} - \\ & \chi_{\mathrm{C{=}C:CN}} - \chi_{\mathrm{CH:CN}} - \chi_{\mathrm{CN:NH}} - 2\chi_{\mathrm{CN:CN}} - \chi_{\mathrm{CN:CC}} - \\ & 2\chi_{\mathrm{CN:NH}} - 5\chi_{\mathrm{CC:CH}} - 5\chi_{\mathrm{CH:CH}}\end{aligned}$$

$$F = -\chi_{\mathrm{CC:CH}} + \chi_{\mathrm{CN:CH}} + 2\chi_{\mathrm{CN:CN}} - \chi_{\mathrm{CH:CH}}$$

The parameters *A*, *B*, *C*, *D*, *E*, and *F* are sufficient to describe all the susceptibility contributions of varying structural environments present in the alkyl β-aminovinyl ketones. The parameter *A* represents end effects in the alkyl β-aminovinyl ketones, and *B* describes the susceptibility contribution of methylene group. The parameter *C* represents branching in the alkyl β-aminovinyl ketones and, therefore, is responsible for the isomeric effects. The parameter *D* accounts for the susceptibility contributions of a functional group in the unsubstituted alkyl β-aminovinyl ketones, and the parameter *E* represents susceptibility contributions of functional group in the substituted alkyl β-aminovinyl ketones. The parameter *F* is an additional parameter and represents interactions in the disubstituted alkyl β-aminovinyl ketones. All these parameters used in the semiempirical calculations have been determined by following the least-square deviation method and are summarized in Table II. Semiempirical diamagnetic susceptibilities have been calculated by the values of parameters and are included in Table I along with the parametric representation of diamagnetic susceptibilities.

It is obvious from the semiempirical calculations that the semiempirically calculated values of diamagnetic susceptibility agree excellently with their corresponding experimental values, as the divergency between semiempirical and experimental diamagnetic susceptibilities is less than 1%. Such an excellent agreement is due to the fact that, in addition to the other structural factors, the effect of the conjugation and the effect of change of hybridization of the orbital of unshared electrons, which have not been duly accounted for in the Pascal, Pacault, and Hoarau method as well as in the wave–mechanical approach, have been duly considered in the form of parameters in the semiempirical calculation, since the parameters, in view of their diamagnetic susceptibility contributions, depend on the nature of the structural environments present in the molecules.

Since the semiempirical approach has provided interesting and encouraging results of diamagnetic susceptibility for the alkyl β-aminovinyl ketones because it considers almost all the structural factors persisting in these molecules and contributing considerably to the molecular diamagnetism, it can be concluded that the semiempirical approach can be applied not only to the simple organic and organometallic compounds but also to the compounds of polyfunctional groups with sufficient accuracy for calculating diamagnetic susceptibilities. Therefore, the semiempirical approach, no doubt, will prove its importance in resolving various existing structural controversies and will add new dimensions to structural chemistry.

Registry No. $CH_3C(O)CH{=}CHNH_2$, 2976-86-5; $CH_3CH_2C(O)CH{=}CHNH_2$, 6140-26-7; $CH_3(CH_2)_2C(O)CH{=}CHNH_2$, 27485-74-1; $i\text{-}C_3H_7C(O)CH{=}CHNH_2$, 27485-75-2; $i\text{-}C_4H_9C(O)CH{=}CHNH_2$, 27526-43-8; $CH_3C(O)CH{=}CHNHEt$, 27485-76-3; $CH_3(CH_2)_2C(O)CH{=}CHNHEt$, 20965-00-8; $CH_3(CH_2)_3C(O)CH{=}CHNHEt$, 27485-78-5; $CH_3C(O)CH{=}CHNMe_2$, 1190-91-6; $CH_3CH_2C(O)CH{=}CHNMe_2$, 6137-82-2; $CH_3(CH_2)_2C(O)CH{=}CHNMe_2$, 6135-08-6; $i\text{-}C_4H_9C(O)CH{=}CHNMe_2$, 18927-45-2; $CH_3C(O)CH{=}CHNEt_2$, 1809-59-2.

Chemical Reactions on Clusters. 3. Gas-Phase Unimolecular Decomposition of $(CH_3)_2O^+$ in Association with Argon Clusters

A. J. Stace*

Contribution from the Department of Chemistry, The University, Southhampton, Hants SO9 5NH, U.K. *Received November 2, 1983*

Abstract: Ion clusters of the type $Ar_n{\cdot}(CH_3)_2O^+$ for n in the range 1–21 have been formed by electron impact following the adiabatic expansion of an argon/dimethyl ether mixture. Despite the apparent fragile nature of these species it is observed that the dimethyl ether ion undergoes extensive unimolecular decomposition without significantly disrupting the argon component of the cluster. The observed product ions are $Ar_n{\cdot}CH_3OCH_2^+$ and $Ar_n{\cdot}CHO^+$. From a detailed experimental study of the factors governing these processes the following conclusions have been drawn: (1) in large clusters excitation of the ether appears to proceed via a charge-transfer mechanism; (2) the excited ether ion decomposes because of the comparatively slow rate of intermolecular energy transfer between it and the argon component; (3) the molecular ion appears to "sit on" the cluster. The results suggest that the ions $Ar_{12}{\cdot}CHO^+$ and $Ar_{18}{\cdot}CHO^+$ are particularly stable; from this observation an analogy has been made between the formation of "magic" numbers of argon atoms and the predicted behavior of small metal clusters.

In two recent publications[1,2] we have presented preliminary results from a series of experiments concerning the unimolecular decomposition of organic ions in association with argon clusters. The general experimental procedure involves the formation of neutral clusters of the form $Ar_n{\cdot}X$. Following electron impact ionization, product ions arising from the unimolecular decomposition of X^+ combined with all or part of the argon component of the cluster are observed. So far approximately 18 examples of this type of behavior have been recorded,[3] ranging from $X = I_2$ to $(CH_3CH_2)_2CO$.

The purpose of this paper is to present the results of a detailed study of the unimolecular decomposition of the dimethyl ether ion in clusters of the type $Ar_n{\cdot}(CH_3)_2O^+$. A mechanism for excitation of the dimethyl ether ion will be proposed, and we also believe that the results presented will substantiate our previous conclusions regarding the position and behavior of the organic ion with respect to the main body of the cluster.[1,2] Briefly these conclusions were (1) the ion "sites on" rather than "within" the cluster,[1] (2) the excited ion decomposes because of the relatively slow rate of intermolecular energy transfer between it and the argon component of the cluster,[1,2] and (3) individual clusters appear to exhibit a phase transition, with the total product ion intensity being dependent upon whether the argon component is in a liquidlike or a solidlike state.[2]

From the nature of the experiment and the provisional conclusions drawn from the results it is possible to identify several related research areas; the results from which may be useful in the interpretation of the present data. The fact that the ion appears to reside on the surface could provide an interesting analogy with small metal clusters and some of their predicted properties.[4,5] Recent IR photodissociation experiments by Gough et al. suggest that CH_3F occupies a surface site in neutral argon clusters.[6] With regard to the competition between intramolecular and intermo-

---

* Present address: School of Molecular Sciences, University of Sussex, Falmer, Brighton, Sussex BN1 9QJ, U.K.

(1) Stace, A. J. *J. Phys. Chem.* **1983**, *87*, 2286.
(2) Stace, A. J. *Chem. Phys. Lett.* **1983**, *99*, 470.
(3) Stace, A. J., unpublished results.
(4) Slater, J. C.; Johnson, K. H. *Phys. Today* **1974**, 34.
(5) Takasu, Y.; Bradshaw, A. M. *Spec. Period. Rep.: Chem. Phys. Solids Their Surf.* **1978**, *7*, 69.
(6) Gough, T. E.; Knight, D. G.; Scoles, G. *Chem. Phys. Lett.* **1983**, *97*, 155.

0002-7863/84/1506-4380$01.50/0