

Interaction of the C=N Bond with the Cyclopropyl Ring

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The conjugative interaction of the C=N bond with the cyclopropyl ring is studied using UV-spectrophotometric technique. The observed small bathochromic shift in the $n\text{-}\pi^*$ bands, relative to the spectra of similar compounds but with no cyclopropyl ring, is attributed to the interaction of the internal Walsh MO with the nonbonded MO of the Nitrogen atom ($\Delta_{\text{int-n}}$ interaction) in the bisected conformation of the molecule. The observed bathochromic shifts of the $\pi\text{-}\pi^*$ bands are explained in terms of the $\Delta\text{-}\pi$ interaction. The gas phase spectra of the azomethine derivatives show vibronic structuring of the band which when analyzed yield wave number differences between the successive vibronic peaks, of the magnitude $720\text{--}860\text{ cm}^{-1}$. They are attributed to the wave number differences between the successive C=N=C deformed ion levels in the excited state.

Introduction

During the last decade various papers appeared dealing with the conjugative interaction of the cyclopropyl ring with unsaturated groups [1–4]. Both experimental and theoretical tools were applied to elucidate the electronic nature of the interaction which had been recognized by the organic chemists before. The studies included interactions with olefinic and aromatic groups as well as with the carbonyl double bond [4]. It was found that the interaction of a cyclopropyl ring with an olefinic group usually increases the energy of the highest occupied π -MO and decreases the energy of the corresponding antisymmetric Walsh molecular orbital (Δ_{as}) of the ring [3]. The interaction with a carbonyl group, however, decreases the energy of its Δ -MO [4]. No such study has appeared yet for the interaction with an azomethine (C=N) bond. In the following we report a UV-spectrophotometric study of this interaction. The spectra of such derivatives, after being synthesized by us, were recorded both in solution and in the gas phase and compared with the spectra of similar derivatives with no cyclopropyl ring.

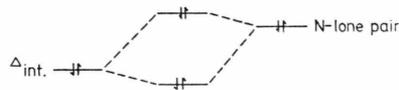
Results and Discussion

A similar scheme of interaction to that of the cyclopropylcarbonyl molecules is expected for the cyclopropyl azomethine derivatives (Figure 1). As

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in the case of the cyclopropyl ketones [4], the bisected conformation is expected for the N-cyclopropyl azomethine derivatives. Such conformation should facilitate the C=N interaction with the antisymmetric Walsh MO (Δ_{as}) and compell an interaction between the lone pair and the internal Walsh MO.

However, due to the big energy difference between both MO's, only a minor increase in the energy of the N-lone pair is expected to result from the interaction.



Thus a small bathochromic shift in the $n\text{-}\pi^*$ UV-band of the azomethine group is expected.

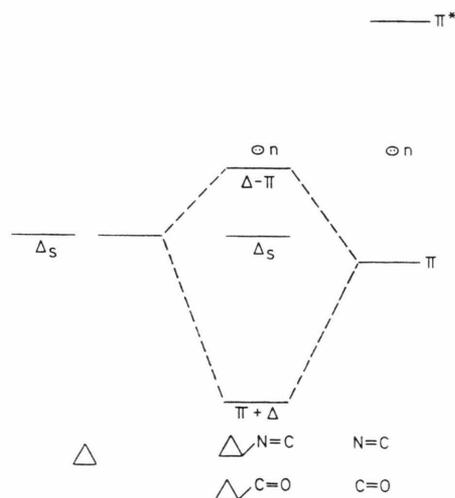
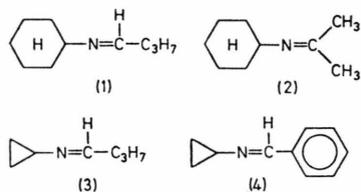


Fig. 1. MO-interaction diagram of the C=O and C=N bonds with the cyclopropyl ring.

The electronic spectra of N-butylidene-cyclohexylamine (1), N-isopropylidene-cyclohexylamine (2), N-butylidene-cyclopropylamine (3) and N-benzylidene-cyclopropylamine (4) were recorded in n-hexane and in methanol solutions as well as in the gas phase. The recorded values of λ_{max} and absorption coefficients are listed in Table 1.

The low values of the absorption coefficients for the first three derivatives indicate their $n\text{-}\pi^*$ nature. The values are of the same order as that of similar azomethine compounds known in the literature [5–10]. Obvious is the red shift of 12 nm in the spectrum of (3) relative to (1). The increase in the wavelength agrees with our assumption of an increase in the N-lone pair energy due to the interaction with Δ_{int} . It is to be recalled that introducing a cyclopropyl ring to the ketones caused hypsochromic shifts in their $n\text{-}\pi^*$ spectra [4]. The difference in behaviour may be viewed in that the lone pair of the carbonyl group is not directly affected by the three membered ring as in the case of (3). The shift in the spectrum of the ketone then is mainly caused by the increase in the energy of the unoccupied $\pi^*\text{-MO}$ [4].



The gas phase spectrum of (1) shows a vibronic structuring (Fig. 1) which when analyzed yield a

Table 1. Measured UV absorption maxima (nm) and the corresponding logarithmic values of the absorption coefficients ($\log \epsilon$) of the azomethine derivatives (1)–(4).

Derivative	Hexane	Methanol	Gas phase
N-butylidene-cyclohexylamine (1)	224–230 (2.264)	223 (2.382)	214 (2.743)
N-butylidene-cyclopropylamine (2)	234 (2.433)	—	226 (2.594)
N-benzylidene-cyclopropylamine (3)	252 (4.156)	254 (4.218)	244 (4.516)
N-isopropylidene-cyclohexylamine (4)	245 (2.298)	230 (2.382)	210 (2.678)

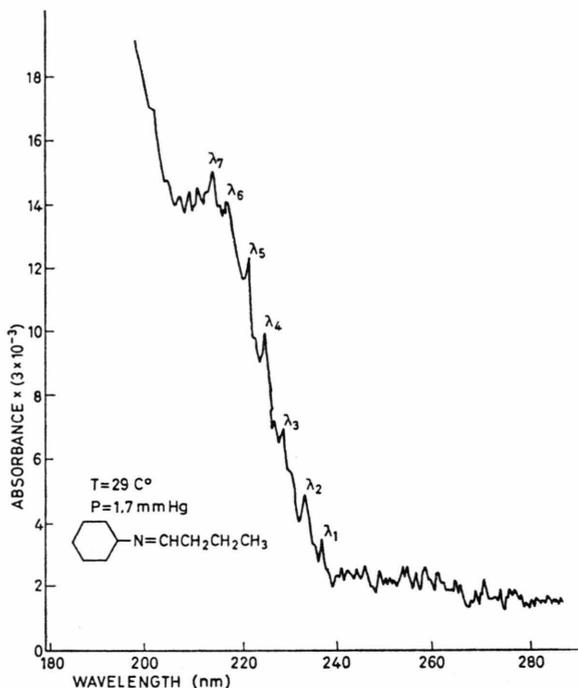


Fig. 2. Gas phase UV-absorption spectrum of N-Butylidene-cyclohexyl-amine (1).

	cm^{-1}
$\bar{\nu}_2 - \bar{\nu}_1$	718
$\bar{\nu}_3 - \bar{\nu}_2$	743
$\bar{\nu}_4 - \bar{\nu}_3$	769
$\bar{\nu}_5 - \bar{\nu}_4$	797
$\bar{\nu}_6 - \bar{\nu}_5$	826
$\bar{\nu}_7 - \bar{\nu}_6$	857

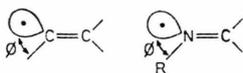
Table 2. Wave number differences between the successive vibronic peaks in the spectrum of N-butylidene-cyclohexylamine.

progression with wave number differences ranging from 718 to 857 cm^{-1} (Table 2). The differences increase in value successively with approximately 25 to 31 cm^{-1} .

The question arises then about the nature of the vibration in the electronic excited state which causes the structuring of the band. In this connection one may exclude the C=N stretching vibration on the basis of the following arguments; the excitation of an electron to the $\pi^*\text{-MO}$ decreases the C=N bond order, as might be seen from simple Hückel arguments. The stretching vibration then should have an intermediate frequency between the known ground state frequencies 1100 cm^{-1} of the C–N bond and 1600 cm^{-1} of the C=N as they are found in the literature [10]. The measured frequencies are too small when compared with these and are more

compatible with a C=N–C deformation frequency (ν_{def}).

Excitation of an n-electron leaves a single electron in the lone pair orbital. The resulting electronic configuration at the radical centre is similar to that of the vinyl radical, the structure of which deviates slightly from linearity [12]. Similar equilibrium structure is expected then for the excited azomethine derivative.



On going to higher deformation levels, i. e. bigger deformation angles (φ), the energy differences increase due to the increasing Repulsion of R with the C=N bond. The increasing values of ν_{def} , as evaluated from the spectrum, correspond then to transitions to the different deformation levels such that the energy differences between each two successive levels increase on going to higher quantum numbers, Figure 3.

A similar spectrum is measured for N-isopropylidene-cyclohexylamine (2). Compared to the azomethine (1) it absorbs at a longer wavelength in solution but a shorter wavelength in the gas phase.

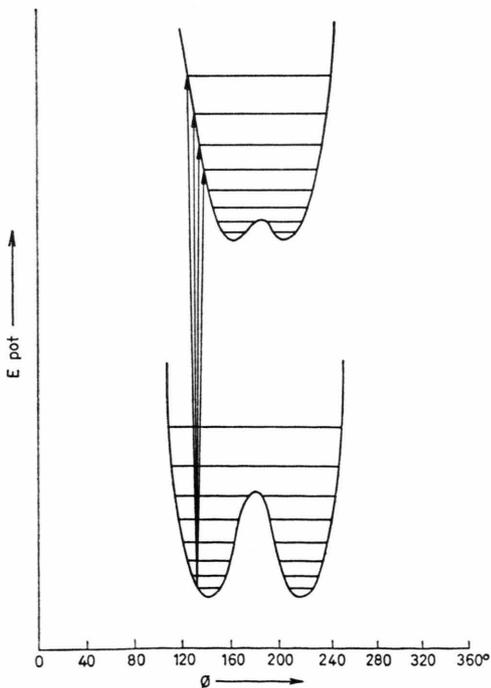


Fig. 3. Transitions to different deformation levels of the azomethine compounds.

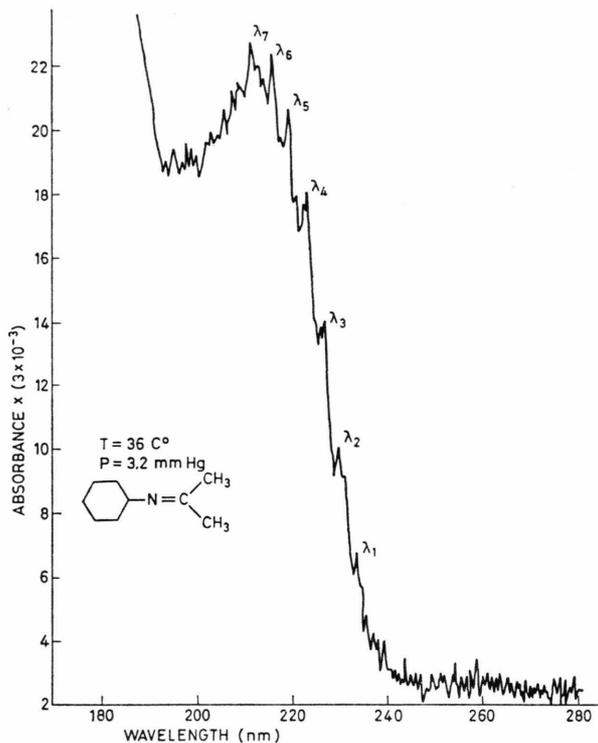


Fig. 4. Gas phase UV-absorption spectrum of N-isopropylidene-cyclohexylamine (2).

	cm ⁻¹
$\tilde{\nu}_2 - \tilde{\nu}_1$	(580)
$\tilde{\nu}_3 - \tilde{\nu}_2$	769
$\tilde{\nu}_4 - \tilde{\nu}_3$	797
$\tilde{\nu}_5 - \tilde{\nu}_4$	826
$\tilde{\nu}_6 - \tilde{\nu}_5$	857
$\tilde{\nu}_7 - \tilde{\nu}_6$	890

Table 3. Wave number differences between the successive vibronic peaks in the spectrum N-isopropylidene-cyclohexylamine (2).

The gas phase spectrum shows a progression similar to that of (1), (Figure 4). The vibronic spacings range from 769 to 890 cm⁻¹ (Table 3), and the subdifferences are 28 to 33 cm⁻¹. The progression may then be similarly attributed to the excitation to different deformation levels (Figure 3).

The high ϵ value in the spectrum of N-benzylidene-cyclopropylamine (4) suggests its assignment to a π - π^* transition. Its λ_{max} shows a bathochromic shift when compared with λ_{max} of N-benzylidene-n-butylamine(5) in ethanol [10]. Second order perturbation treatment shows an increase in the energy of the π -HOMO of the benzylidene group in (4) relative to (5), which could cause a red shift in λ_{max} of the system.

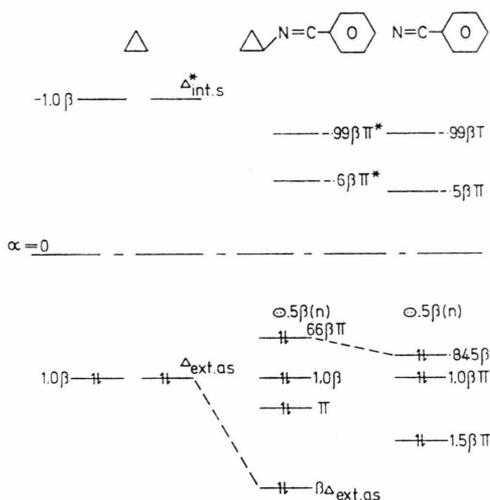


Fig. 5. Perturbation interaction diagram of the Walsh orbitals with the π -MOs in benzylidene azomethine.

The gas phase spectra of (3) and (4) showed no resolvable vibronic structuring, possibly due to the low vapour pressure of the compounds.

IR Spectra

The most significant vibrations in the IR spectra of the studied molecules are the $\nu_{C=N}$ stretching (1650 cm^{-1}) and the two antisymmetric cyclopropyl vibrations (1020 and 1040 cm^{-1}), Table 4. Inspect-

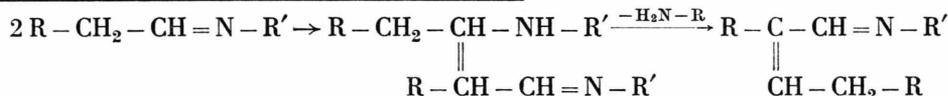
ing the values in the table one notice the $\nu_{C=N}$ of (1), 1663 cm^{-1} , is equivalent to that of (2) but higher than the frequency of (3), 1660 cm^{-1} . Obviously, the difference is caused by the conjugation to the cyclopropyl ring.

Still lower is the frequency of (4), 1638 cm^{-1} , where the azomethine bond is conjugated to both cyclopropyl and phenyl rings. Also a positive charge on the azomethine bond increases the $\nu_{C=N}$ frequency as is seen from the value of the silveriodide complex (9).

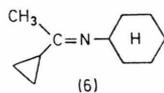
Experimental Section

The used reagents were supplied by Fluka AG, Buchs, Switzerland, and purified before the reaction. The IR spectra were measured with a Beckman, IR 4250 spectrophotometer, the UV spectra with a Beckman Acta M VII spectrophotometer and the NMR spectra with a Varian A-60-A instrument. The C, H, N analysis were carried out by Alfred Bernhardt laboratories, Elbach über Engelskirchen, W. Germany.

The azomethine derivatives of the aldehydes were synthesized through direct condensation of the aldehyde with the amine using benzene as dehydrating agent. As it is known in the literature [13] the so formed azomethine derivatives undergo easily an aldol type condensation.



Azomethine(9) was synthesized via its AgI complex according to the Kuhn's method [14]. An attempt to synthesize methyl, cyclopropylidene-cyclohexylamine(6) was unsuccessful due to the fast hydrolysis of the liberated base.



Typical signals for the azomethine protons were noticed on measuring the NMR spectra of the azomethine derivatives (Table 5). The chemical shifts are in the range of the values published by Parry *et al.* [15], the $-\overset{\text{H}}{\text{C}}=\text{N}$ proton appearing at 7.6–8 ppm and the $-\overset{\text{H}}{\text{N}}=\text{C}-\text{R}$ proton at 2.5–3.2 ppm

for aliphatic R and 4.6 ppm for aromatic R. All measurements were done in CCL_4 solutions with TMS as standard.

N-butylidene-cyclohexylamine (1)

7.3 ml (0.06 mol) cyclohexylamine were added to 5.8 ml (0.06 mol) butylaldehyde dissolved in 40 ml methylene chloride. The exothermally reacting mixture was then refluxed for one hour using a soxhlet containing a 4 Å molecular sieve and a condenser sealed with a CaCl_2 tube. As then the methylene chloride was distilled and the residue vacuumdistilled under a reduced pressure of nitrogen. The fraction at $60^\circ\text{C}/4\text{ mm}$ was collected to yield 4 g (40% of the theoretical yield) of *N*-butylidene-cyclohexylamine (1).

Table 4. Measured wave numbers for $\nu_{\text{C=N}}$ stretching and the two antisymmetric cyclopropyl vibrations.

	$\nu_{\text{C=N}}$ (cm^{-1})	Ring- deformation (cm^{-1}) (e)	
N-butylidene-cyclohexylamine (1)	1663	—	
N-butylidene-cyclopropylamine (3)	1660	1025	1043
N-benzylidene-cyclopropylamine (4)	1638	1030	1050
N-isopropylidene-cyclohexylamine (2)	1663	—	
N-isopropylidene-cyclohexylamine silver iodide complex (9)	1670	—	
N-(2-ethylhexen-2-ylidene)-cyclohexylamine (7)	1640	—	
N-(2-ethylhexene-2-ylidene)-cyclopropylamine (8)	1650 (1625)	1020	1040

Table 5. H-NMR chemical shifts measured for the synthesized azomethine derivatives (τ , ppm).

	$\left(\begin{array}{c} \text{H} \\ -\text{C}=\text{N} \end{array} \right)$	(C=N—C—H)
N-butylidene-cyclohexylamine (1)	7.6 (t)	2.9 (m)
N-(2-ethylhexene-2-ylidene)-cyclohexylamine (7)	7.75 (s)	2.63 (m)
N-butylidene-cyclopropylamine (3)	7.75 (t)	—
N-isopropylidene-cyclohexylamine (2)	—	2.08 (m)
N-benzylidene-cyclopropylamine (4)	8.19 (s)	2.9 (m)

	C	H	N
Calc.	78.30	12.47	9.13
Found	78.66	11.88	8.88
$n_{\text{D}}^{25} = 1.4608$			

A second fraction was collected at 110 °C/4 mm to yield 3.5 g N-(2-ethyl, hexene-2-ylidene)-cyclohexylamine (7).

	C	H	N
Calc.	81.10	12.10	6.78
Found	80.76	11.88	7.15

N-butylidene-cyclopropylamine (3)

The same method as that of (2) was used with 4 ml (0.04 mol) butylaldehyde, 40 ml methylene chloride and 3.2 ml (0.05 mol) cyclopropylamine. The yield was 2.3 g of (3) (46% of the theory), distilled at 210 °C/8 mm.

	C	H	N
Calc.	75.67	11.71	12.61
Found	75.85	11.58	12.40
$n_{\text{D}}^{25} = 1.446$			

A second fraction was collected at 38 °C/0.3 mm yielding 1.0 g N-(2-ethylhexene-2-ylidene)-cyclopropylamine (8).

	C	H	N
Calc.	79.90	11.57	8.47
Found	79.93	11.30	8.04

N-benzylidene-cyclopropylamine (4)

7.3 ml (0.07 mol) benzaldehyde in 40 ml methylene chloride and 4.2 ml (0.06 mol) cyclopropylamine were reacted in a similar manner as that of the two previous reactions. The product was distilled under N_2 at 68 °C/0.6 mm yielding 8 g (80% of the theoretical yield) of (4).

	C	H	N
Calc.	82.75	7.58	9.65
Found	82.93	7.54	9.63
$n_{\text{D}}^{25} = 1.556$			

N-isopropylidene-cyclohexylamine-silver iodide complex (6)

150 ml of 50% aqueous solution of HI [16] were added dropwise to 25 ml (0.22 mol) cyclohexylamine in a three neck flask fitted with a stirrer and a reflux condenser. The water was then removed under vacuum and the residue washed several times with ether, filtered and dried under vacuum. 48 g of the salt were obtained melting at 192–194 °C. 14 g (0.059 mol) silver iodide, 6 g (0.028 mol) cyclopropylammonium iodide and 8 ml dimethylformamide were mixed in a 250 ml flask and gently heated with stirring till the salts dissolved. After cooling the solution to 0 °C, 100 ml ice cold acetone

were added gradually to it. The formed mixture was then kept three days at -17°C after which a white precipitate was formed. It was filtered, washed three times with dry ether and dried under vacuum. 16 g of the disilver iodide complex (6) were obtained (80% of the theoretical yield), $\text{C}_9\text{H}_{18}\text{N}^+ \cdot 2 \text{AgI} \cdot \text{I}^-$.

	C	H	N
Calc.	14.66	2.11	1.79
Found	14.60	2.40	1.85

N-isopropylidene-cyclohexylamine (2)

6 g KCN dissolved in 10 ml 2 N NaOH solution were added to a mixture of 12 g (0.02 mol) silver-

iodide complex (6) and 25 ml ether in a separatory funnel and then immediately and intensively shaken. The ether layer was then separated and the aqueous solution extracted three times with 50 ml ether portions. The combined ether extracts were then dried over 4 A molecular sieve for 24 hours. After distillation of the ether the product was then vacuum distilled under nitrogen. 2 g 28% of the theoretical yield) of *N*-isopropylidene-cyclohexylamine (2), boiling at $32^{\circ}\text{C}/1.7 \text{ mm}$ were collected.

	C	H	N
Calc.	77.69	12.23	10.07
Found	77.51	12.21	10.14
$n_D^{25} = 1.465$			

- [1] M. Shanshal, *Z. Naturforsch.* **27a**, 1665 (1972).
 [2] E. Heilbronner, R. Gleiter, T. Hoshi, and A. de Meijere, *Helv. Chim. Acta* **56**, 1594 (1973).
 [3] See R. Gleiter, *Topics in Current Chemistry* **86**, 199 (1979).
 [4] J. A. Al-Khafaji and M. Shanshal, *Z. Naturforsch.* **30a**, 1023 (1975).
 [5] D. A. Nelson and J. J. Worman, *Tetrahedron Lett.* **1966**, 507.
 [6] A. E. Gillan and E. S. Stern, *Electronic Spectroscopy*, Edward Arnold, London 1957, p. 56.
 [7] J. J. Worman, G. L. Pool, and W. Jensen, *J. Chem. Educ.* **47**, 709 (1966).
 [8] D. A. Nelson, J. J. Worman, and R. L. Atkins, *J. Colo.-Wyo. Acad. Sci.* **5**, 42 (1966).
 [9] H. H. Jaffe and M. Orchin, *Theory and Application of UV-Spectroscopy*, J. Wiley & Sons, New York 1962, p. 105.
 [10] S. Patai, *The Chemistry of Carbon-Nitrogen Double Bond*, Interscience, J. Wiley & Sons, London 1970.
 [11] See [4] and references therein.
 [12] M. Shanshal, *Z. Naturforsch.* **26a**, 1336 (1971).
 [13] E. C. Wagner, *J. Org. Chem.* **19**, 1862 (1954).
 [14] R. Kuhn and H. Schretzmann, *Chem. Ber.* **90**, 557 (1957).
 [15] K. W. Parry, P. J. Robinson, P. J. Sainsbury, and M. J. Waller, *J. Chem. Soc. B*, **1970**, 700.
 [16] A. Vogel, *Practical Organic Chemistry*, 3rd Edition, Longman, London 1972.