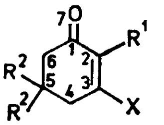
Calculation of Molecular Geometries of Some Halogeno- and Piperidino-cyclohexenones by Dipole Moment Analysis

By **D. Pitea** *† and **G. Favini**,† Istituto di Chimica Fisica, Università, 95125 Catania, Italy

The electric dipole moments of some halogeno- and piperidino-cyclohexenones are reported and discussed in comparison with the corresponding αβ-unsaturated ketones. The dipole moment values support the view that in the cyclohex-2-enone series the vinyl-carbonyl system is coplanar, whereas in the 5,5-dimethyl derivatives steric interaction between the 5(*ax*)-methyl and the carbon atoms of the –C=C–C=O system may occur. They yield no definite evidence regarding the structures of the 2-methyl derivatives.

KINETIC results[1] of nucleophilic substitution on 3-halogenocyclohex-2-enones (Ia)—(IIIa) and (IIb) by



(I) $R^1 = R^2 = H$ a; $X = Cl$
(II) $R^1 = H, R^2 = Me$ b; $X = Br$
(III) $R^1 = Me, R^2 = H$ c; $X =$ Piperidine

piperidine have shown that 3-chlorocyclohex-2-enone (Ia) reacts faster than 3-chloro-5,5-dimethylcyclohex-2-enone (IIa). This lack of reactivity seems to depend on a different geometric configuration of the two substrates. An examination of scale models shows that the introduction of a 5(*ax*)-methyl in (Ia) results in steric interference opposing the coplanar configuration of the conjugated C=C–C=O system.

In connection with our programme of kinetic studies, further information was required on the geometric configuration of these substrates. Electric dipole moments of compounds (Ia)—(IIIa), (IIb), and (Ic)—(IIIc) have been measured. A theoretical analysis has also been made.

EXPERIMENTAL

Almost all the substituted cyclohex-2-enones were purified by preparative g.l.c., and a Carlo Erba Fractovap model GV was used for this purpose.

3-*Halogenocyclohex*-2-*enones*.—These compounds were prepared from the corresponding cyclohexane-1,3-diones (commercial samples) by reaction with PCl_3 or PBr_3 in

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† *Present address:* Istituto di Chimica Fisica dell'Università, Milano, Italy.

[1] D. Pitea and G. Favini, *J.C.S. Perkin II*, in the press.

anhydrous chloroform as described.[2–9] The resulting crude oil was distilled through a short Vigreux column under reduced pressure and the separated halogeno-derivative was purified by preparative g.l.c. using a 2 m × 10 mm column packed with WEAS (20%) coated on Chromosorb P (30—60 mesh). This procedure afforded: *3-chlorocyclohex-2-enone* (Ia), colourless oil, b.p. 58 °C at 2 mmHg, n_D^{25} 1·5172 (lit.,[5] 1·5008) (Found: C, 55·1; H, 5·8. C_6H_7ClO requires C, 55·2; H, 5·4%); *3-chloro-5,5-dimethylcyclohex-2-enone* (IIa), colourless oil, b.p. 109 °C at 14 mmHg, n_D^{25} 1·5066 (lit.,[9] 1·4935) (Found: C, 60·5; H, 6·8. $C_8H_{11}ClO$ requires C, 60·55; H, 7·0%); *3-bromo-5,5-dimethylcyclohex-2-enone* (IIb), colourless oil, b.p. 121 °C at 25 mmHg, n_D^{25} 1·5191 (lit.,[9] 1·5202) (Found: C, 47·15; H, 5·65. $C_8H_{11}BrO$ requires C, 47·3; H, 5·45%); *3-chloro-2-methylcyclohex-2-enone* (IIIa), pale yellow oil, b.p. 60 °C at 2 mmHg, n_D^{25} 1·5145 (Found: C, 58·35; H, 6·4. C_7H_9ClO requires C, 58·15; H, 6·25%).

3-Piperidinocyclohex-2-enones.—A solution of the corresponding cyclohexane-1,3-dione (0·03 mol) and piperidine (0·03 mol) in benzene (100 ml) was refluxed in an apparatus connected to a Dean–Stark head. As soon as the calculated volume (0·5 ml) of water had been collected, the solvent was evaporated and the residual red oil was extracted with light petroleum (b.p. 40—60°) by a liquid–liquid extractor.

The solvent was evaporated and the solid or liquid piperidino-derivative residue was recrystallized from light petroleum (b.p. 40—60°) or separated by distillation through a short Vigreux column under reduced pressure and purified by preparative g.l.c. using a 2 m × 10 mm column packed with SE 30 (20%) coated on Chromosorb P (30—60 mesh). These procedures afforded the following compounds: *3-piperidinocyclohex-2-enone* (Ic), pale yellow oil, b.p. 135 °C at 0·08 mmHg (Found: C, 73·5; H, 9·55; N, 7·8. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·55; N, 7·8%) which was also obtained as white crystals (from light petroleum b.p. 40—60°) with m.p. near room temperature; *3-piperidino-5,5-dimethylcyclohex-2-enone* (IIc), white crystals, m.p. 89 °C (from light petroleum, b.p. 40—60°) (Found: C, 75·3; H, 10·2; N, 6·6. $C_{13}H_{21}NO$ requires C, 75·3; H, 10·2; N, 6·75%); *3-piperidino-2-methylcyclohex-2-enone* (IIIc), pale yellow oil, n_D^{25} 1·5734 (Found: C, 74·5; H, 10·05; N, 7·25. $C_{12}H_{19}NO$ requires C, 74·55; H, 9·9; N, 7·25%).

Dipole Moments.—Electric dipole moments were determined by measuring the dielectric constants, refractive indices, and specific volumes of benzene solutions at 25 ± 0·05 °C. For dielectric constant measurements a Dipolmeter W.T.W. model DM01 equipped with a gold-plated DFL1 measuring cell was used; the sensitivity, $\Delta\varepsilon/\varepsilon$, was of the order of 10^{-5} at 2 MHz. The refractive indices were measured by a Bausch–Lomb Abbe refractometer to $\pm 3 \times 10^{-5}$. The specific volumes were measured by a 10 ml Ostwald pycnometer calibrated by use of the solvent, which was filled from the dielectric cell immediately after the dielectric measurement had been made.

The equation of Halverstadt and Kumler[10] was used to calculate solute molar polarization ($_\infty P_2$) at infinite dilution, assuming the following solvent properties[11] at 25 °C: dielectric constant (ε_1) 2·2725; specific volume (V_1) 1·1445. Molar refractions (R_D) for the sodium D line were obtained from measured refractive indices of solutions;[12] no allowance was made for atomic polarization. For compound (Ia) the R_D value was calculated from the refractive index and density of the pure substance.[5] The solute molar electronic polarizations (P_E) were also calculated from the electronic polarization of cyclohex-2-enone ($P_E = 27{\cdot}24$),[13] plus a value for each substituent; the latter was taken from

TABLE 1 *

$10^5 w_2$	$10^5(\varepsilon_{12} - \varepsilon_1)$	$10^5(V_{12} - V_1)$	$10^5(n_{12}^2 - n_1^2)$
3-Chlorocyclohex-2-enone (Ia)			
237	2125	−70	
495	4475	−149	
533	4806	−159	
709	6399	−218	
1018	9189	−307	
3-Chloro-5,5-dimethylcyclohex-2-enone (IIa)			
253	1819	−82	32
440	3098	−144	57
539	3830	−175	68
698	4913	−228	88
1001	7163	−326	125
3-Bromo-5,5-dimethylcyclohex-2-enone (IIb)			
237	1265	−103	12
423	2335	−186	24
598	3340	−262	36
728	4029	−316	45
964	5453	−423	60
3-Chloro-2-methylcyclohex-2-enone (IIIa)			
83	510	−51	39
129	787	−80	69
174	1084	−108	90
255	1547	−159	129
294	1789	−182	150
3-Piperidinocyclohex-2-enone (Ic)			
208	5305	−65	58
444	10,829	−139	122
614	15,193	−192	172
857	21,312	−268	240
1032	26,288	−322	286
3-Piperidino-5,5-dimethylcyclohex-2-enone (IIc)			
225	4838	−62	62
413	8624	−114	115
551	11,690	−153	144
687	14,516	−191	180
965	20,583	−267	248
3-Piperidino-2-methylcyclohex-2-enone (IIIc)			
69	1088	−30	35
110	1791	−48	56
188	3245	−83	
200	3399	−88	101
284	4885	−125	
380	6651	−167	191
538	9405	−237	271

* w = Weight fraction; ε_1 and ε_{12} are the dielectric constants for solvent and solution respectively, V_1 and V_{12} are the corresponding specific volumes, and n_1 and n_{12} the corresponding refraction indices.

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TABLE 2 *

Compound	$d\varepsilon/dw$	$-dV/dw$	dn^2/dw	P_2/cm^3	R_D/cm^3	P_E/cm^3	μ/D
(Ia)	$9{\cdot}04 \pm 0{\cdot}01$	$0{\cdot}305 \pm 0{\cdot}003$		237·3	32·56	31·96	$3{\cdot}41 \pm 0{\cdot}01$
(IIa)	$7{\cdot}15 \pm 0{\cdot}05$	$0{\cdot}326 \pm 0{\cdot}001$	$0{\cdot}124 \pm 0{\cdot}001$	209·7	41·79	41·04	$3{\cdot}20 \pm 0{\cdot}03$
(IIb)	$5{\cdot}73 \pm 0{\cdot}04$	$0{\cdot}438 \pm 0{\cdot}002$	$0{\cdot}066 \pm 0{\cdot}001$	216·5	44·65	43·74	$3{\cdot}26 \pm 0{\cdot}02$
(IIIa)	$6{\cdot}05 \pm 0{\cdot}04$	$0{\cdot}623 \pm 0{\cdot}002$	$0{\cdot}513 \pm 0{\cdot}010$	151·7	36·78	36·50	$2{\cdot}72 \pm 0{\cdot}03$
(Ic)	$25{\cdot}4 \pm 0{\cdot}3$	$0{\cdot}312 \pm 0{\cdot}001$	$0{\cdot}279 \pm 0{\cdot}002$	847·4	53·26	53·44	$6{\cdot}44 \pm 0{\cdot}05$
(IIc)	$21{\cdot}3 \pm 0{\cdot}1$	$0{\cdot}277 \pm 0{\cdot}001$	$0{\cdot}249 \pm 0{\cdot}003$	822·2	62·56	62·53	$6{\cdot}34 \pm 0{\cdot}03$
(IIIc)	$17{\cdot}8 \pm 0{\cdot}1$	$0{\cdot}440 \pm 0{\cdot}001$	$0{\cdot}502 \pm 0{\cdot}001$	628·2	58·42	57·98	$5{\cdot}54 \pm 0{\cdot}02$

* Errors in $d\varepsilon/dw$, dV/dw, and dn^2/dw are quoted as ± probable errors [15] and based on the least-squares plot. These errors are combined to give the quoted error in μ.

tabulated [14] values of bond electronic polarizations. The values agree to within 1 cm^3. Results are reported in Tables 1 and 2.

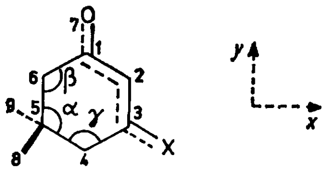
CALCULATIONS

The theoretical analysis has been carried out by estimating separately the σ- and π-contribution to the dipole moment. In the calculations the following assumptions were made.

(1) The σ-dipole contributions were calculated as vector sum of the bond moment values M (A–B): †

A–B	C–H	C_{sp^3}–C_{sp^2}	C–O	C–Cl	C–Br
M	0·00 [16]	0·30 [16]	0·80 [17]	1·59 [16]	1·56 [16]

The μ_σ for the C_{sp^2}-piperidine group was derived in the following way. Dipole moment values of 1-methylpiperidine [18] and 1-phenylpiperidine [19] are in good agreement, both in magnitude and direction, with those of trimethylamine [20] and *NN*-dimethylaniline [21] respectively. Then, to a first approximation, it should be possible to assume for the π-dipole component in 1-phenylpiperidine the same value estimated [22,23] for the true mesomeric moment in *NN*-dimethylaniline. From this latter and the gross moment of 1-phenylpiperidine, the μ_σ value for the C_{sp^2}-piperidine group can be found; it is estimated to be 1·21 D ($\mu_\sigma = 0{\cdot}56\mathbf{i} - 0{\cdot}33\mathbf{j} + 1{\cdot}02\mathbf{k}$, where **i**, **j**, and **k** denote unit vectors directed along the positive directions of the *x*, *y*, and *z* axes, respectively, in the Figure).



(2) The π-dipole contributions were calculated by the HMO method.

The values of the Coulomb (α_i) and resonance (β_{ij}) integrals given by Bonnet and Cocordano [24] were used for the vinyl-carbonyl core C=C–C=O:

$$\alpha_7 = \alpha + 0{\cdot}7\,\beta$$
$$\alpha_1 = \alpha + 0{\cdot}2\,\beta \qquad \beta_{17} = 1{\cdot}1\,\beta$$
$$\alpha_2 = \alpha + 0{\cdot}1\,\beta \qquad \beta_{12} = 0{\cdot}5\,\beta$$
$$\alpha_3 = \alpha + 0{\cdot}1\,\beta \qquad \beta_{23} = \beta$$

When X = halogen, the following parameters were used:

$$\alpha_{Cl} = \alpha + 1{\cdot}7\,\beta \qquad \beta_{CCl} = 0{\cdot}5\,\beta$$
$$\alpha_{Br} = \alpha + 1{\cdot}4\,\beta \qquad \beta_{CBr} = 0{\cdot}5\,\beta$$

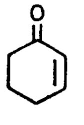
According to Julg's treatment,[25] previously applied to $\alpha\beta$-unsaturated ketones,[26] the parameters were corrected to take into account the perturbating effect of the substituents and of the ring, the latter being replaced by two methyl groups in positions 6 and 4.

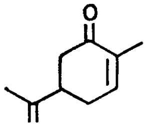
When the heteroatom X was the piperidine nitrogen, the parameters $\alpha_N = \alpha + 1{\cdot}47\beta$ and $\beta_{CN} = 1{\cdot}05\beta$ have been selected as the most reasonable values fitting the π-contribution to the dipole moment of 1-phenylpiperidine.

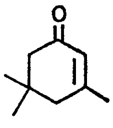
(3) To the best of our knowledge there are no structural data on the interatomic distances of vinyl-ketones; therefore, the following bond lengths were chosen: r_{CO} 1·227, $r_{C_1C_2}$ 1·471, and $r_{C_2C_3}$ 1·337 Å as estimated from bond orders in cyclohex-2-enone; r_{CCl} 1·718, r_{CBr} 1·86, r_{CN} 1·43, $r_{C(sp^2)C(sp^3)}$ 1·505 and $r_{C(sp^3)C(sp^3)}$ 1·533 Å were selected as standard values. All valence angles in the vinyl-carbonyl system were assumed to be 120°.

RESULTS AND DISCUSSION

In the cyclohex-2-enone series (I) the dipole moment values are greater than those in the corresponding 5,5-dimethylcyclohex-2-enone series (II). These differences are significant and may also be found in dipole moments of analogous $\alpha\beta$-unsaturated ketones such as cyclohex-2-enone (IV) ($\mu = 3{\cdot}62$ D [27]), carvone (V) ($\mu = 3{\cdot}17$ D [17]),


(IV)


(V)


(VI)

and isophorone (VI) ($\mu = 4{\cdot}02$ D [28] in carbon tetrachloride; 3·96 D [29] in dioxan).

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† The convention here used to define bond moment is that A is the positive end of the dipole in M (A–B).

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The experimentally observed decrease in dipole moment can be accounted for by the following explanations.

αβ-*Unsaturated Ketones*.—Calculations were made by assuming coplanarity of the vinyl-carbonyl skeleton and the results for the π- and σ-components and the total moments are collected in Table 3.

TABLE 3

Calculated π, σ, and total dipole moments of αβ-unsaturated ketones

Compound	Component	$\mu(x)$/ D	$\mu(y)$/ D	$\mu(z)$/ D	μ_{calc}/ D	μ_{exp}/ D
(IV)	π	−0·25	2·54		3·65	3·62[a]
	σ	0·52	1·10			
(V)	π	−0·26	2·24		3·19[b]	3·17[c]
	σ[b]	0·26	0·95			
(VI) $\omega_{12} = 0°$	π	−0·31	3·04		4·29	
	σ	0·26	1·25			4·02[d]
$\omega_{12} = 30°$	π	−0·34	2·70	0·77	4·03	3·96[e]
	σ	0·20	1·14	0·48		

[a] From ref. 27. [b] Estimated by neglecting the moment of the MeC⁚CH$_2$ group. [c] From ref. 17. [d] From ref. 28. [e] From ref. 29.

The total calculated moment of cyclohex-2-enone (IV) agrees well with the experimental one; the direction of this moment can also be estimated by an analysis of the vector difference between cyclohex-2-enone and cyclohexanone ($\mu = 3·08$ D[2]) moments. The difference between the σ-components can be easily calculated. That between the π-components will make only a small angle with the *y*-axis (see Figure), *i.e.* in cyclohex-2-enone the $\mu_\pi(x)$ is very small compared with the $\mu_\pi(y)$; moreover $\mu_\pi(x)$ will be negative and $\mu_\pi(y)$ positive. Then, a relation $\mu_\pi(x) = -k\mu_\pi(y)$, with small *k* values, holds between $\mu_\pi(x)$ and $\mu_\pi(y)$. The calculations for different *k* values in the range 0·05—0·15 give almost no change for the μ_π and a mean value $\boldsymbol{\mu}_\pi = -0·25\mathbf{i} + 2·51\mathbf{j}$ results, in good agreement with that reported in Table 3. From the geometry that will be reported later, the σ-component was also calculated using the method suggested by Del Re and Berthod-Pullman.[30] The estimated value $\boldsymbol{\mu}_\sigma = 0·14\mathbf{i} + 0·89\mathbf{j} + 0·01\mathbf{k}$ is smaller than that calculated from bond moments; taking into account the inaccuracy of the two methods there is reasonable agreement between the two values.

The calculated moment for the 2-methylcyclohex-2-enone is not directly comparable with the true moment; however, it is in agreement with the experimental moment of carvone (V) if, owing to the free rotation around the C_{sp^2}–C_{sp^3} axis, the contribution of the isopropenyl group to the total moment is small.

The actual moment of isophorone (VI) is smaller than the calculated one. This discrepancy may be explained if we admit that the vinyl-carbonyl skeleton is not coplanar for steric reasons.[31] *A priori*, the steric strain can be relieved either by twisting around the essentially single bond (ω_{12}) or by twisting around the essentially double bond (ω_{23}) or, finally, by a conrotatory or disrotatory twisting around the two bonds.

The ω_{23} and disrotatory possibilities have been rejected as they cause an increase in dipole moment. In the other two cases the dipole moment values at different interplane angles are smaller than the value of 4·29 D calculated on the assumption of a coplanar vinyl-carbonyl skeleton. Only for the ω_{12} twist, however, are the strains in the α, β, and γ valence angles small; for $\omega_{12} = 30°$ a good agreement with the experimental dipole moment is obtained (Table 3).

We shall have to consider whether the twist angle can be justified by steric reasons. For this purpose, the steric crowding between the 5(*ax*)-methyl and the carbon atoms C(1), C(2), and C(3) has been estimated.

For the coplanar configuration of the vinyl-carbonyl skeleton, from the previously reported geometrical data, we obtain: $\alpha = 105°$, $\beta = 108°$, $\gamma = 110·5°$ while C(5) is 0·78 Å above the *xy* plane. The methyl groups have been treated as pseudo-atoms X localized at the middle of the normal from the plane of the hydrogens to the carbon atom (r_{XC} 1·702 Å). Using Hendrickson's relation[32] to estimate the C(8)–C(5)–C(6) angle (110·3°), the distances between 5(*ax*)-methyl and C(1), C(2), and C(3) are found to be 2·97, 3·14, and 3·00 Å, respectively. These values are all smaller than the touching distance (*d* 3·6 Å) as determined from the van der Waals radii.[33]

The following values are obtained for the twisted configuration with $\omega_{12} = 30°$: $\alpha = 116·2°$, $\beta = \gamma = 113·3°$. The C(8)–C(5)–C(6) angle is estimated to be 108·7° and the distances between the 5(*ax*)-methyl and C(1), C(2), and C(3) are 3·60, 3·71, and 3·30 Å, respectively; the latter is slightly less than the touching distance.

These calculations seem to justify the $\omega_{12} = 30°$ angle even apart from any strict energetic treatment and to support the evidence from dipole moment analysis.

TABLE 4

Calculated π, σ, and total dipole moments of 3-halogenocyclohex-2-enones

Compound	Component	$\mu(x)$/ D	$\mu(y)$/ D	$\mu(z)$/ D	μ_{calc}/ D	μ_{exp}/ D
(Ia)	π	−0·55	2·80		3·39	3·41
	σ	1·90	0·31			
(IIa)[a]	π	−0·58	2·48	0·75	3·20	3·20
	σ	1·83	0·19	0·48		
(IIb)[a]	π	−0·70	2·63	0·76	3·29	3·25
	σ	1·81	0·21	0·48		
(IIIa)	π	−0·55	2·51		2·88	2·73
	σ	1·64	0·16			

[a] Values for the twisted configuration with $\omega_{12} = 30°$ (see text).

3-*Halogenocyclohex*-2-*enones*.—The same preferred geometry assigned to each αβ-unsaturated ketone was applied to the corresponding 3-halogenocyclohex-2-enones. Results are given in Table 4.

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It can be seen that the calculated dipole moments for derivatives (Ia), (IIa), and (IIb) are very close to the experimental ones. The validity of the result for compound (IIIa) is not quite so clear owing to the uncertainty in the conformation of the corresponding αβ-unsaturated ketone.

3-*Piperidinocyclohex*-2-*enones*.—The dipole moment calculations for derivatives (Ic) and (IIc) were made by assuming that they contain the piperidine ring as a ' chair ' to which the cyclohexenone group, being large, is attached by an equatorial bond.[18,19,34] For derivative (IIIc) an examination of a scale model clearly shows steric interference between the piperidine ring and the 2-methyl group: as a result, the conformation may be affected in many ways. Tentatively, calculations were made for a coplanar vinyl-carbonyl group by twisting the piperidine ring through an angle θ about the C–N single bond. The results are summarized in Table 5.

For derivatives (Ic) and (IIc) the actual moments are greater than the calculated ones, but the relative values are in agreement. The difference in the absolute values could be due to an inadequate selection of the parameters for μ_π calculations. When this difference is taken into account, an angle of twist θ *ca.* 30° can be estimated for derivative (IIIc).

In conclusion, analysis of the dipole moments supports the view that in compounds (Ia), (Ic), and (IV) the vinyl-carbonyl system is coplanar, whereas it is twisted through *ca.* 30° about the C(1)–C(2) bond in compounds (IIa), (IIb), (IIc), and (VI). For derivatives (IIIa), (IIIc), and (V) the evidence is uncertain.

TABLE 5

Calculated π, σ, and total dipole moments of 3-piperidinocyclohex-2-enones

Compound	Component	$\mu(x)$/D	$\mu(y)$/D	$\mu(z)$/D	μ_{calc}/D	μ_{exp}/D
(Ic)	π	−1·80	5·26	−0·30	6·12	6·44
	σ	1·08	0·77	1·02		
(IIc) [a]	π	−1·76	4·79	0·53	5·87	6·34
	σ	1·02	0·66	1·50		
(IIIc) θ = 0°	π	−1·86	5·17	−0·30	5·93	5·54
	σ	0·82	0·62	1·02		
θ = 30°	π	−1·37	4·04	−0·17	5·16	
	σ	1·08	1·07	0·89		
θ = 60°	π	−0·69	2·69	−0·04	4·15	
	σ	1·27	1·39	0·51		
θ = 90°	π	−0·21	1·80	0·00	3·50	
	σ	1·34	1·51	0·00		

[a] Values for the twisted configuration $\omega_{12} = 30°$ (see text).

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