Organic Spectroscopy and its Relationship to Ground-state Chemistry

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Summary Conformational analysis of spectral properties (u.v. and c.d.) of ten amino-cyclohexanones shows that two ways exist in which the two functional groups can interact through σ bonds: their relationship to reactivity in Grob fragmentation is shown.

THE relationship between the accelerated rate of solvolysis of some $\gamma\delta$ unsaturated toluene-*p*-sulphonates and the charge-transfer $\pi \rightarrow \pi^*$ band of the corresponding ketones[1] or Grob fragmentation[2] and the σ-coupled transition of the corresponding β-amino-ketones[3] have been commented on; both effects appear to be dependent very strictly on the relative orientations of the π-orbital on the γ-carbon (or the lone pair on nitrogen) and the orientation of the leaving group or one of the lobes of the π-orbital on the carbonyl carbon. As c.d. (and o.r.d.) are governed by the same electronic interactions as u.v. spectra[4–6] we decided to analyse empirically the spectroscopic properties of the available α- and β-amino- and -azido-cyclohexanones.†

The conclusions of our analysis of the compounds tabulated below are as follows:

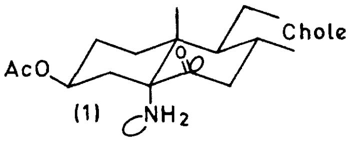
(i) A part of the red shift in the $n \rightarrow \pi^*$ transition is the result of coupling of the π and π^* energy levels with σ and σ^* levels of the C–N bond when these can interact, *i.e.* α axial or β equatorial, *i.e.* in a W arrangement by coupling through σ-bonds (Compounds 4, 5, 6, and 9). This effect attenuates quickly as the number of C–C bonds increases, being negligible when $n = 3$.

(ii) The remainder of the red shift in the $n \rightarrow \pi^*$ transition arises when the lone pair on N is *trans*-diaxial to the C_α–C=O bond when N is attached to α-carbon (Compounds 1 and 3) (in a W arrangement to one of the lobes of the π-orbital on the carbonyl carbon) or when the lone pair is *trans*-diaxial to the C_α–C_β bond when N is on the β-carbon (Compounds 4, 7, and 9).

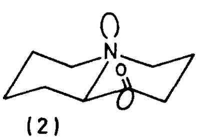
(iii) When condition (ii) is fulfilled, the transition probability of the $n \rightarrow \pi^*$ transition is enhanced (ϵ *ca* 50—80; compounds 3, 4, and 9—this does not apply to compound 7 as it is symmetrical). Also, a new band appears at lower wavelengths which was described as due to a σ-coupled transition.[3] Probably a better description is a split $\pi \rightarrow \pi^*$ transition by coupling with the nitrogen lone pair, the lower-energy component being shifted to 220—240 nm.[5]

(iv) When the lone pair on the α-N atom is *cis* to the C_α–C=O bond (compound 2) or the lone pair on the β-N atom is *cis* to the C_α–C_β bond (compounds 5, 6, and 8) the transition probability of the $n \rightarrow \pi^*$ transition is not enhanced. The same will apply when the C–N bond on the β-carbon is axial, *i.e.* *cis* to the C_α–C=O bond (compound 10).

(v) The change in λ_{max} in c.d. approximately follows conditions (i) and (ii).



(1)



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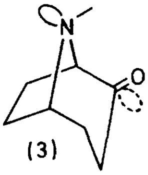

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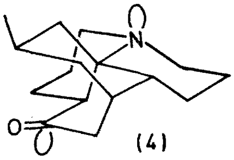

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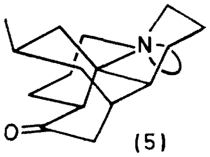

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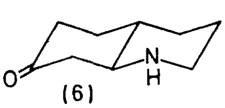

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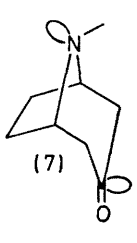

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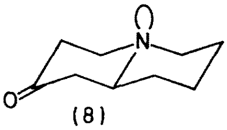
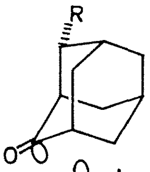
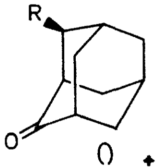


(8)



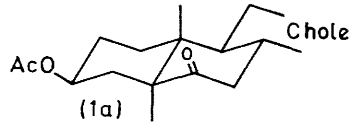
(9) R = N–$\overset{+}{N}_2$

(9a) R = Me



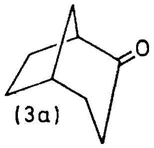
(10) R = N–$\overset{+}{N}_2$

(10a) R = Me

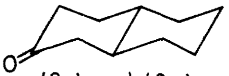


(1a)

(2a)



(3a)



(6a) and (8a)

(vi) Octant-like behaviour of the $n \rightarrow \pi^*$ transition can be expected when condition (iii) is fulfilled (compounds 1, 3, 4, and 9); the $\pi \rightarrow \pi^*$ transition will have opposite chirality to that of the $n \rightarrow \pi^*$ transition.

(vii) Antioctant behaviour of the $n \rightarrow \pi^*$ transition will be observed only when condition (iv) is satisfied (compounds 2, 5, 6, 8, and 10). (See also Ref. i, Table).

(viii) When the lone pair on N is removed by protonation, the change from octant to antioctant (compound 4) or increased antioctant behaviour is

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† Although alkyl azides have the same symmetry as O (or S‡), compounds (9) and (10) were used because there are no β-amino-compounds available that illustrate the β-axial orientation.

observed (compounds 5 and 6), the $n \rightarrow \pi^*$ transition loses its intensity and a part of its red shift and the split $\pi \rightarrow \pi^*$ transition disappears (compounds 4, 7).

It can be seen from this analysis that two functional groups (such as a carbonyl group and a nitrogen) can interact in two ways, depending on their relative orientations, through C–C bonds.‡ These give rise to different spectral characteristics which, in turn, reflect their ground-state properties such as chemical reactivity, conformational stability, and spectroscopic properties (i.r.).

Interproton coupling *via* the bonding electrons is much better understood theoretically;[6] if the lone pair on nitrogen and one of the lobes of the orbital on the carbonyl carbon that interacts with it as stated in condition (ii) were replaced by protons, long-range coupling between those protons would be observed.[6]

When the NH_2 group in compound (1) is replaced by a hydroxy-group, a red shift in λ_{max} is observed, but only small enhancement of the $n \rightarrow \pi^*$ transition. However, it contribution to $\Delta\epsilon$ in c.d. is only slightly octant-like, and sometimes even antioctant.[8] Similarly, the oxa- and thia-analogues of (7) show only spectral properties that would be expected from direct addition of the two chromophores. Thus it should not be surprising that 4-tetrahydropyranyl and 4-tetrahydrothiopyranyl tosylates exhibit retarded rates of solvolysis.[9] This difference in behaviour is due to the orbital symmetry of O and S. When it is changed, ROH → $[RO]^-$ Grob fragmentation is again observed.[10]

TABLE*

Compound	U.v. λ_{max} (nm)	U.v. ϵ	C.d. λ_{max} (nm)	C.d. $\Delta\epsilon$	Solvent	Ref.
(1)			310	−7·07	Dioxan	a
(2)	300	37	300	−1·42	Iso-octane	b, c
(3)	314	68	319	−2·4	Ethanol	d, e
	228	500	228	+4·1		
(4)	284	68	289	+4·39	Ethanol	f
	221	1520	228	−6·66		
(4) HCl	277	43	285	−0·6	Ethanol	f
(5)	282	34	290	−1·02	Ethanol	f
(5) HCl				>−1·26†	Ethanol	f
(6)	286	19	288	+0·01	Methanol	g
(6) HCl			294	−0·44	Chloroform	g
(7)§	230	650	opt.	inact.	Ethanol	h
(7) HCl	284	22	opt.	inact.	Ethanol	h
(8)	295	17	296	+0·44	Iso-octane	b, i
(9)	293	69	304	+1·30	Dioxan	j
(10)			294	−0·34	Dioxan	j
(1a)			*ca.* 288	−3·87	Methanol	k
(2a)	280	43		+1·00	Methanol	l
	293	26			Iso-octane	
(3a)	287	18	297	+0·84	Dioxan	m
(6a) & (8a)				+1·35	Methanol	n
(9a)	290	27	300	+0·78	Dioxan	j
(10a)	288	23	303	+0·09	Dioxan	o

* Compounds in the "a" series are the carbocyclic analogues of the amino-ketones; they are quoted for comparison purposes. Both series have the same absolute stereochemistry. In some instances o.r.d. data were converted into c.d. using the equation $a = 40{\cdot}3\ \Delta\epsilon$.

Compounds (3) and (3a) deserve comment. It may appear that (3) is "antioctant" in comparison with (3a). However, it must be realised that the N atom in (3) is in a negative octant and if it behaves in an octant manner, its contribution will be greater than that of the ethano-bridge.

† Converted from o.r.d. curve which has not reached the second extremum.

§ The $n \rightarrow \pi^*$ transition is not visible being weak because of symmetry.

[a] G. Snatzke and A. Veithen, *Annalen*, 1967, **703**, 159; [b] S. F. Mason, K. Schofield, and R. J. Wells, *J. Chem. Soc.* (*C*), 1967, 626; [c] S. Yamada and T. Kunieda, *Chem. and Pharm. Bull.* (*Japan*), 1967, **15**, 490; [d] R. C. Cookson, *Proc. Roy. Soc.*, 1967, *A*, **297**, 27; [e] S. Archer and R. M. Bell, *J. Amer. Chem. Soc.*, 1960, **82**, 4642; [f] W. A. Ayer, B. Altenkirk, R. H. Burnell, and M. Moinas, *Canad. J. Chem.*, 1969, **47**, 449; [g] R. A. Johnson, H. C. Murray, L. M. Reinecke, and G. S. Fonken, *J. Org. Chem.*, 1968, **33**, 3207. We thank Dr. R. A. Johnson for a gift of this compound and Professor W. Klyne for the measurement of its c.d. Some of the spectral data were remeasured at Southampton on compounds kindly supplied by Professor W. A. Ayer; [h] J. Devonshire, Ph.D. Thesis, Southampton, 1969; [i] The absolute configuration of (8) was reversed from that in Ref. b for the purpose of ready comparison with (8a). N atom shows some predicted antioctant behaviour [weaker than (5)] even though it is in the nodal plane of the carbonyl group. This means that the perturbation of the C_α–C_β bond by a β-equatorial alkyl substituent reduces the symmetry of the 4-piperidone ring; [j] G. Snatzke and G. Eckhardt, *Tetrahedron*, 1968, **24**, 4543; [k] J. W. Blunt, M. P. Hartshorn, and D. N. Kirk, *ibid.*, 1965, **21**, 559; [l] C. Djerassi and J. Staunton, *J. Amer. Chem. Soc.*, 1961, **83**, 736; [m] H. M. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, p. 988; [n] C. Djerassi and W. Klyne, *J. Chem. Soc.*, 1963, 2390; [o] G. Snatzke, B. Ehrig, and J. Klein, *Tetrahedron*, 1969, **25**, 5601.

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‡ A theoretical treatment of coupling through bonds has already been given;[7] our empirical derivation of the favoured geometries is in agreement. Of course, other factors play an important role in these interactions such as the relative energies of the π,π^* C=O orbitals, σ, σ^* C–N orbitals, and the n-orbital of N (and the symmetry of the substituent in the case of O and S). This can be seen in protonation of the lone pair on N; the increase in energy of the N–H orbital relative to the n-orbital of N prohibits coupling.

Other examples of Grob fragmentation bear a direct relationship to the spectroscopic properties discussed above.[2,11]

The generalisation of these principles and their application to various chemical concepts such as neighbouring group participation, conformational stability, anomalies in conformational analysis, and a reappraisal of the Octant Rule and its various "reverse" Octant sub-rules is in preparation.

(*Received, April 21st,* 1970; *Com.* 584.)

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[1] S. Winstein, L. de Vries, and R. Orloski, *J. Amer. Chem. Soc.*, 1961, **83**, 2020.

[2] C. A. Grob, H. R. Kiefer, H. J. Lutz, and H. J. Wilkens, *Helv. Chim. Acta*, 1967, **50**, 416.

[3] R. C. Cookson, J. Henstock, and J. Hudec, *J. Amer. Chem. Soc.*, 1966, **88**, 1060.

[4] N. L. Allinger, J. C. Tai, and M. A. Miller, *J. Amer. Chem. Soc.*, 1966, **88**, 4495.

[5] A. Moskowitz, A. E. Hansen, C. L. Forster, and K. Rosenbeck, *Biopolymers, Symposia*, No. 1, 1964, 75.

[6] L. M. Jackman and S. Sternhell, "Applications of N.M.R. Spectroscopy in organic Chemistry," Pergamon, London, 1969, p. 312.

[7] R. Hoffman, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499.

[8] G. Snatzke and A. Veithen, *Annalen*, 1967, **703**, 159; C. Djerassi, O. Halpern, V. Halpern, O. Schindler, and C. Tamm, *Helv. Chim. Acta*, 1958, **41**, 250.

[9] D. S. Tarbell and J. R. Hazen, *J. Amer. Chem. Soc.*, 1969, **91**, 7657.

[10] P. S. Wharton and G. A. Hiegel, *J. Org. Chem.*, 1965, **30**, 3254.

[11] C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1.