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H.M.O. CALCULATIONS ON [4,5c]-FUROTROPONE AND RELATED SYSTEMS

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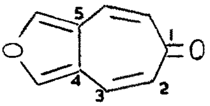
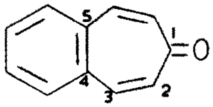
In a forthcoming paper (1) the preparation of [4,5c]-furotropone (I) is described and its chemical and spectral properties are compared with those of 4,5-benztropone (II) and tropone. Whilst the two bicyclic systems are shown to be comparable in themselves, they have appreciably less aromatic character than tropone. The reported (2) resonance energy of benztropone (85 kcals/mole) should therefore be regarded with suspicion.

I



II



In the present paper, results of H.M.O. calculations (TABLE) on the three systems are shown to support these conclusions.

The calculations, using the paremeters recommended by Streitwieser (3), indicate that the charge density on the carbonyl oxygen and the single bond character of the carbonyl group increase in the order [4,5c]-furotropone, 4,5-benztropone, tropone. The trend does not appear to be dependent on the parameters chosen. The results for tropone are similar to those reported by Brown (4) for an earlier Huckel calculation but differ from those obtained by SCF methods (5). The latter show a considerable decrease in the charge on oxygen and more marked bond alternation compared with Hückel Theory. However for a comparison of the properties of the three systems the Hückel method is probably quite adequate. The variation in the carbonyl bond order in the series is in accordance with the variation in the carbonyl stretching frequency in the infra red spectra. Since a criterion for aromaticity in these systems is the development of a delocalised system with a highly polarised carbonyl bond, the M.O. results would suggest that tropone is the more aromatic system.

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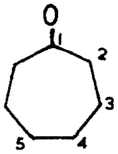
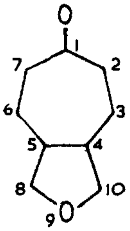
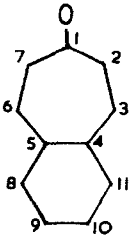
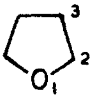
TABLE

System	Bond	Bond Order	νC=O cm-1	Atom	Electron Density	Chem Shift τ
	0-1	0.534	1582	0	1.735	
	1-2	0.540		1	0.830	
	2-3	0.705		2	0.926	
	3-4	0.599		3	0.889	3.05
cf. Ref (4)	4-5	0.688		4	0.903	
	0-1	0.580	1599	0	1.684	
	1-2	0.509		1	0.795	
	2-3	0.758		2	1.038	3.48
	3-4	0.491		3	0.848	2.63
	4-5	0.420		4	1.046	
	4-10	0.710		8	0.951	1.94
	9-10	0.420		9	1.756	
	0-1	0.569	1590	0	1.696	
	1-2	0.515		1	0.804	
	2-3	0.749		2	0.978	3.35
	3-4	0.507		3	0.865	2.73
	4-5	0.517		4	0.960	
	5-8	0.579		8	0.978	2.53
	8-9	0.703		9	0.970	
	9-10	0.618				
				1	1.791	
				2	1.015	2.58
				3	1.090	3.63
C_6H_6					1.000	2.73

In contrast to the uniform charge density distribution in the tropone ring, the electron density at C-2 is significantly greater than at C-3 in the bicyclic systems. Charge alternation of this type might be expected to confer properties characteristic of α,β-unsaturated ketones on these systems, and this is consistent with their ready formation of oximes and dinitrophenylhydrazones, a property not shared by tropone.

A comparison of the chemical shifts of the protons in the seven membered rings of [4,5c]-furotropone and 4,5-benztropone must involve considerations of the changes in π- charge and ring current (6,7). The chemical shifts of the C-2 and C-3 protons of I and II are of the same order as the chemical shift of the protons of tropone, implying that there is a ring current in the seven membered rings of these two compounds. In both cases the lines attributed to the C-3 proton occur at lower field than those from the C-2 proton, as would be expected from the smaller π charge at C-3, and the greater deshielding of the proton at this position resulting from the ring current in the non-troponoid part of the molecule.

The difference in the chemical shifts of the C-2 protons in I and II is in agreement with the calculated charge densities.

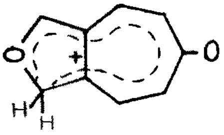
When comparing the chemical shifts of the C-3 protons in I and II there are two major factors to be considered. The lower electron density of C-3 in I relative to II would cause a relative downfield shift of the C-3 proton signal in the former. However the greater ring current in the non-troponoid ring of II compared with that of I should cause a relative downfield shift of the C-3 proton of II.

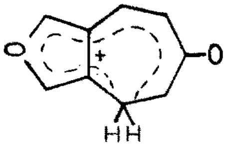
The two effects are probably of the same order of magnitude but since they are not accurately known, further discussion on the difference in the chemical shift of C-3 proton signals in I and II does not seem meaningful.

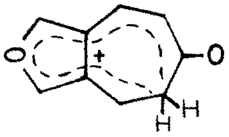
The shift to lower field of the "furan proton" in I and the benzenoid protons in II, relative to the chemical shift in the parent compounds may be attributed to both ring current and charge density effects.

The NMR spectrum of [4,5c]-furotropone in concentrated sulphuric acid (1) is consistent with protonation occurring on the carbonyl oxygen, though a small amount of protonation at other sites is not precluded. Indeed, in concentrated deuteriosulphuric acid, deuterium is exchanged for the hydrogen on the furan ring.

That protonation at this site should be favoured over protonation at C-2 or C-3 is in complete accord with the calculated Hückel energies of the systems III, IV and V


III


IV


V

The protonated species III is more stable than IV or V by over 0.3β

The calculations were performed on the Birmingham University KDF9 computer. We wish to thank Dr. E. J. Forbes for his comments and the S.R.C. for Research Studentships.

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