Unusual Carbonyl Infrared Band in a New Mesoionic System

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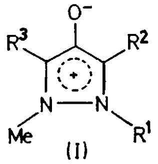
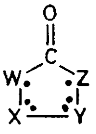
Summary The carbonyl i.r. band of 1,2-dimethyl-3,5-diphenylanhydro-4-hydroxy-1,2-diazolium hydroxide (Ia) (1545 cm^{-1} in Me_2SO) was identified by its large solvent shift which correlates linearly with a large solvent shift in the u.v. spectrum.

Two substituted examples (Ia) and (Ib) of the new mesoionic system, anhydro-4-hydroxy-1,2-diazolium hydroxide, and crystalline monohydrates of (Ic—g) have been prepared by two basically different routes.† There are no previous reports of this system in anhydrous form, although substances corresponding to monohydrates of (Ih) and Ii) have been reported.[2,3]

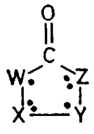


(I)

	a	b	c	d	e	f	g	h	i
R^1	Me	Ph	Me	Me	Ph	Me	Ph	Ph	Ph
R^2	Ph	Ph	H	Me	Me	Me	Ph	H	Me
R^3	Ph	Ph	H	Me	Me	Ph	Me	H	H



(II)



(III)

W,X,Y, and Z = groups in conjugated heteroaromatic ring contributing the indicated number of electrons to the π cloud.

The system exhibits large solvent shifts in its u.v./visible spectrum [*e.g.* (Ia) λ_{max} C_6H_6, 447; Me_2SO, 421; $CHCl_3$, 410; Bu^{t}OH, 370; MeOH, 345; H_2O, 325 nm)]. For most pure solvents the frequency shift is proportional to the shift observed by Dimroth *et al.*[4] for another mesoion, and plots of shifts *versus* molarity of alcohol for $CHCl_3$–ROH mixtures are similar in shape to those observed by Saxena, Stafford, and Stafford[5] for a related mesoion.

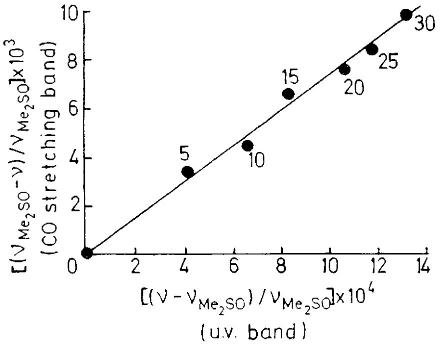


Figure. *Relationship between the relative shifts of the* CO *stretching band and the long wavelength band of* (Ia) *in* D_2O–Me_2SO. *Percentage compositions of the solvent* (*w/w* D_2O *in* Me_2SO) *are indicated against each point. Above* 30% *the slope of the curve decreases.*

The CO stretching vibration of (Ia) does not appear in the usual carbonyl region, but was identified[6] as the band exhibiting the largest shift in changing from aprotic to protic solvent (1546 cm^{-1} in Me_2SO, 1531 cm^{-1} in 30% w/w D_2O in Me_2SO). The assignment was supported by the linear correlation (Figure) between the i.r. and u.v. solvent shifts of (Ia), similarly observed for simple carbonyl com-

† Reported in part in ref. 1.

pounds by Ito and his co-workers.[7] This relationship is thought[6,8] to occur because both shifts are directly dependent on the strength of the hydrogen bond between the oxygen atom and the solvent.

The low value of the CO stretching frequency of (Ia) is in marked contrast to the usual value for 5-membered mesoionic compounds such as sydnones (1750—1770 cm^{-1}). However, compounds (I) correspond to the general type (II), whereas most 5-membered mesoionic systems are of type (III) which would be expected to have different bond order patterns.

The only other examples of (II) in the literature are some tetrazoles[9] for which no i.r. data are published, but an analogous tetrazole system (II) bearing a sulphur in place of the exocyclic oxygen has been studied by *X*-ray crystallography,[10] and the CS bond appears to be intermediate in length between double and single. It is of interest to note that a ring opened keten resonance structure as suggested[11] by Thiessen to explain the high wavenumber of the carbonyl i.r. band of sydnones is not possible for compounds of type (II), for which, if there is a weak bond it should lie between atoms XY.

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