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SYMMETRICALLY BIFURCATE HYDROGEN BONDING—III[1] (*sym*-o,o′ DIACYL)-DIPHENYLAMINES

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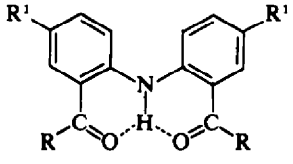
Abstract—Symmetrically bifurcate three-centre hydrogen bonding, N—H⋯O, was found in several (*sym*-o,o′-diacyl)-diphenylamines, $[o(\text{-R—CO—}C_6H_4)]_2NH$.

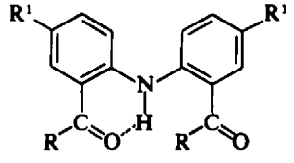
Bifurcate hydrogen bonding, in which the proton of a group A—H may be co-ordinated by two or more proton acceptor centres B, seems to be of considerable interest both from the theoretical point of view and because of its possible occurrence in biological systems. In previous work carried out in this laboratory,[1,2] intramolecular symmetrically-bifurcate hydrogen bonding was found in several bis-(β-acylvinyl)amines, $[R^1\text{—CO—}CR^2\text{=}CH]_2NH$, where R^{-1} denotes alkyl or phenyl and R^2 stands for alkyl or hydrogen. Compounds containing this type of bonding incorporated into an aromatic system are now discussed.

(*sym*-o,o′-Diacyl)-diphenylamines can form the corresponding bis-chelate **1a** and can also assume structures **1b** or **1c** in which bifurcate hydrogen bonding is not involved; NMR and IR spectra investigated. These are (*sym*-o,o′-diformyl)-diphenylamine (**1**; R′ = R = H), (*sym*-o,o′-diacetyl)-diphenylamine (**1**; R′ = H, R = CH_3) and (*sym*-o,o′-dibenzoyl-p,p′-dimethyl)-diphenylamine (**1**; R′ = CH_3; R = Ph). To ensure unambiguous spectral assignments it was necessary to differentiate the effects of conjugation and of hydrogen bonding upon the IR frequencies. Accordingly, the model compounds with expectedly similar electron distribution but incapable of forming the double chelate, *viz.*, (o,p′-diformyl)-diphenylamine (**2**; R = H) and (o,p′-diacetyl)-diphenylamine (**2**; R = CH_3) were also investigated. Evidently, only two isomers (**2a** and **2b**) are possible for these model compounds.

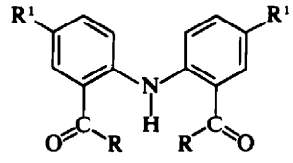
The essential IR data obtained in the temperature range −20 to +70° are presented in Table 1 and



1a



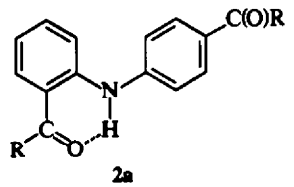
1b



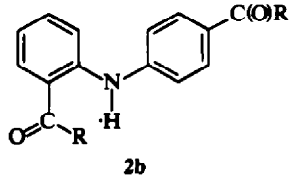
1c

should enable the differentiation between these forms.[cf. 1]

The possibility of occurrence of intramolecular bifurcate hydrogen bonding of non-symmetrical type was discussed more than 20 years ago by Ospenson[2] in connection with the problem of structure of azo dyes. Symmetrical bifurcation was postulated by Urbanski[3] for some amino nitro compounds, but no convincing evidence was offered.



2a



2b

RESULTS AND DISCUSSION

Three aromatic compounds capable of forming the symmetrically bifurcate hydrogen bonding were synthesized and their IR and NMR spectra

Table 1. Wave numbers (in cm^{-1}) of the main IR absorption bands of diacyldiphenylamines and their intensity changes at different temperatures[a]

Compound	ν_{N-H}	IR bands $\nu_{C=O}$ I	II	III
1, R = R′ = H	3268	1695 sh[b]	1688[c]	1667[b]
2, R = H	3284	1704		1669
1, R = CH_3; R′ = H	3240	1680 sh[b]	1668[c]	1648[b]
2, R = CH_3	3260	1683		1653
1, R = C_6H_5; R′ = CH_3	3280	1668[b]	1647[c]	1637[b]

[a]0·001 M and 0·01 M solutions in carbon tetrachloride for ν_{N-H} and $\nu_{C=O}$, respectively. [b]At 29°; intensity increased at +70° and decreased at −20°. [c]At +29°; intensity decreased at +70° and increased at −20.

representative IR and NMR spectra are shown in Figs 1–3.

None of these compounds exhibits the stretching frequency of the free amino group which means that structure **1c** and structure **2b** must be excluded from consideration. It is not possible, however, to distinguish between **1a** and **1b** on the ground of the N—H stretching vibration as the frequency differences between a singly and doubly hydrogen bonded N—H group are very small.[1]

The carbonyl absorption of compounds **1** occurs at three frequencies, labelled I, II, and III, which can be assigned convincingly on the basis of temperature measurements and of the spectra of the model compounds **2**. Thus, the higher of the two carbonyl frequencies (frequency I) of the model compounds, i.e. 1704 cm^{-1} in (**2**; R = H) and 1683 cm^{-1} in (**2**; R = CH_3) (Fig 1) can be assigned unequivocally to the free p′-carbonyl group; hence, the highest of the three carbonyl frequencies of compound **1** is ascribed here to the free carbonyl group of structure **1b**. The correctness of the above assignment is corroborated by the decrease in intensity of this absorption at low temperatures and its increase at elevated temperatures, as the hydrogen bonded conformer **1a** is the more stable (see Fig 2).

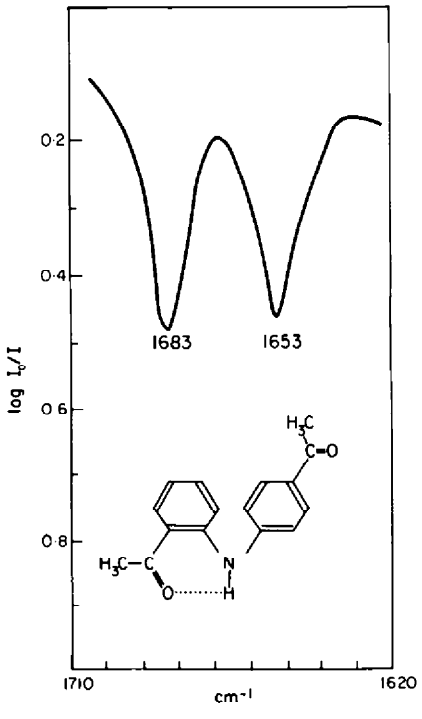


Fig 1. IR spectrum of compound (**2**; R = CH_3), 0·01 M solution in CCl_4. Cell thickness: 1 mm.

The low-frequency band III, which is also common to all the compounds **1** and **2** and behaves like band I when varying the temperature, is assigned to the hydrogen-bonded carbonyl group in the chelated part of the molecule of **1b**.

The central band II, which occurs in **1** but not in **2** and which changes its intensity in a reverse manner than is the case with bands I and III, is undoubtedly due to the stretching vibrations of the carbonyls engaged in the symmetrically-bifurcate hydrogen bonding of the double chelate of **1a**. The less pronounced lowering of the carbonyl frequency upon hydrogen bonding as compared with band III is readily explicable since both electron transfer from nitrogen to oxygen and the effect of the hydrogen atom is shared in this case by two carbonyl groups. It should be mentioned that band II and III were not resolved in the spectra of bis-(β-acylvinyl)amines.[1]

NMR is less conclusive than IR. There is one amino proton signal for **1**, one aldehyde proton signal for (**1**; R = R¹ = H) and one methyl signal for (**1**; R = CH_3; R¹ = H), no splitting being observed even at −100°C (Fig 3). Hence, the lifetime of **1a** and **1b** is too short on the NMR timescale to permit direct observation. Nevertheless, the distinctly higher shift of the amino proton signal

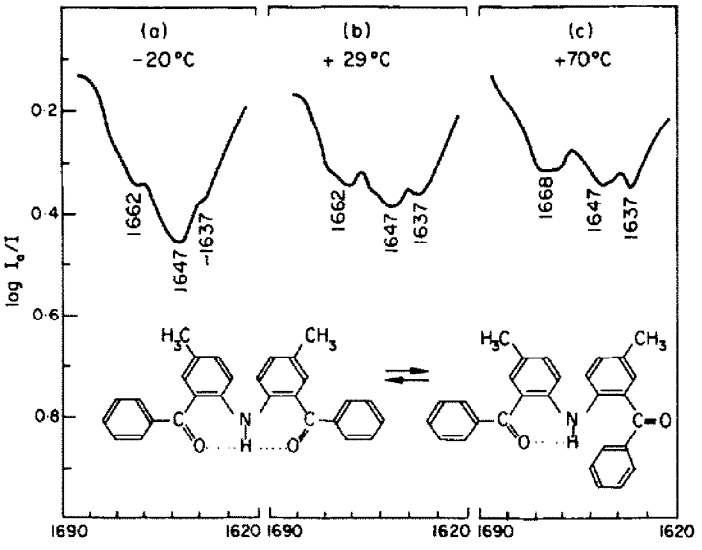


Fig. 2. IR spectra of compound (1; $R^1 = CH_3$; R = Ph); 0·01 M solution in CCl_4. Cell thickness: 1 mm (a) Sample temperature −20°; (b) + 29°; (c) + 70°.

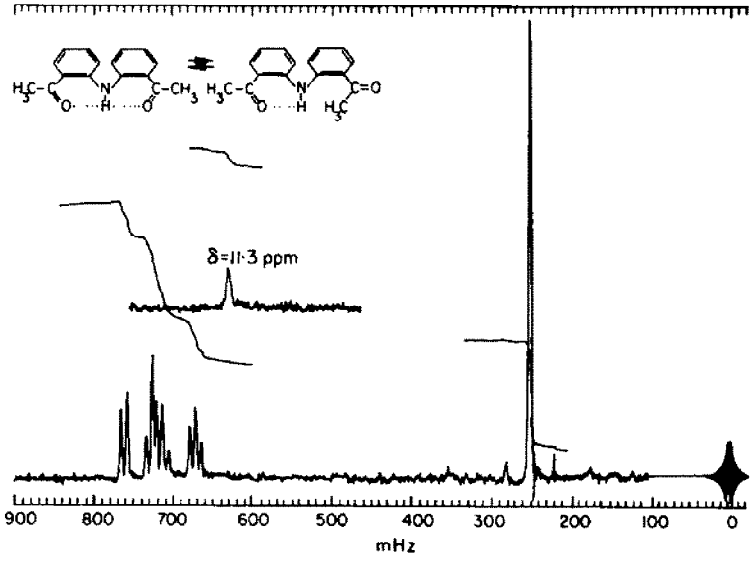
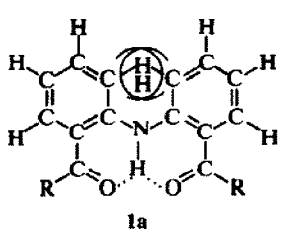


Fig 3. NMR spectrum of compound (1; R′ = H; R = CH_3). *Ca.* 7% solution in CCl_4.

in (1; R = R^1 = H) (10·9 ppm) and (1; R = CH_3; R′ = H) (11·3 ppm) than in (2; R = H) (10·2 ppm) and (2; R = CH_3) (10·3 ppm), respectively, points indirectly[1] to a contribution of the form **1a**. The lesser stability of the double chelate **1a** in (*sym*-o,o′-diacyl)-diphenylamines as compared with that observed for bis-(β-acylvinyl)-amines can be explained by non-planarity of the molecules of the former group of compounds. Indeed, the repulsion between the aromatic hydrogens adjacent to nitrogen is much stronger than in the case of the corresponding vinylic hydrogens.

It should be mentioned again[1] that the spectral data demonstrate the symmetrical structure of the



1a

molecule as a whole, leaving open the question of whether there is one central minimum or rather two symmetrically located minima for the bridged amine hydrogen. However, CNDO calculations[4] on bis-(β-acylvinyl)-amines resulted in a potential surface with one deep central minimum and two insignificant shoulders.

EXPERIMENTAL

All compounds were obtained by Ullmann condensation of suitably substituted anilines and bromobenzenes under condition similar to those employed by Jensen and Retwisch,[5] and Coldberg and Kelly.[6] Thus, compound (1; R = R¹ = H) was obtained from o-aminobenzaldehyde and o-bromobenzeldehyde, compound (2; R = H) from o-aminobenzaldehyde and p-bromobenzaldehyde, (1; R¹ = CH_3; R = H) from o-aminoacetophenone and o-bromoacetophenone, (2; R = CH_3) from o-aminoacetophenone and p-bromobenzaldehyde, and (1; R¹ = CH_3; R = Ph) from 3-benzoyl-p-toluidine and 3-benzoyl-4-bromotoluene. Equimolar amounts of the substrates were refluxed for 5 h in amyl alcohol [in the case of (1, R = H) and (2; R = H)] or nitrobenzene [(1, R¹ = H; R = CH_3), (2; R = M), and (1; R¹ = CH_3; R = Ph)] with 5 moles of anhydrous potassium carbonate and a small amount of freshly prepared copper dust. Solvent and unreacted substrates were removed by steam distillation and the residue was extracted with ether. The ether was evaporated from the dried solution and the product was purified by crystallization and sublimation. The yields, melting points and elemental analyses are given in Table 2.

IR spectra were measured on a Carl Zeiss-Jena UR-20 (1700–1600 cm^{-1}) and Unicam SP-700 (above 3000 cm^{-1}) spectrometer. A Unicam thermostated cell was used for measurements in the 1700–1600 cm^{-1} region. Carbon tetrachloride POCh (Gliwice, Poland) analytical grade was carefully dried before use.

NMR spectra of *ca* 7% solutions in carbon tetrachloride were measured at 100 MHz on a JEOL-100-4H spectrometer.

Table 2. Yields, melting points (uncorrected) and analyses of diacyldiphenylamines 1 and 2

			Analyses					
			calc			found %		
	Yield (%)	M.p. (°C)	C	H	N	C	H	N
(1; R′ = R = H) $C_{14}H_{11}NO_2$	20	98–100	74·67	4·89	6·22	74·75	4·99	6·02
(2; R = H) $C_{14}H_{11}NO_2$	2[a]	82–83	74·67	4·89	6·22	75·10	5·15	6·11
(1; R′ = H; R = CH_3) $C_{16}H_{15}NO_2$	50	113–115	75·89	5·93	5·53	75·88	5·97	5·62
(2; R = CH_3) $C_{16}H_{15}NO_2$	62	122–123	75·89	5·93	5·53	75·89	5·83	5·53
(1; R′ = CH_3; R = Ph) $C_{28}H_{23}NO_2$	15	172–175	82·93	5·68	3·46	83·10	5·87	3·49

[a]Yield of pure product deduced by TLC.

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REFERENCES

[1]Part II; J. Dabrowski and Z. Swistun, *J. Chem. Soc.* (*B*), 818 (1971)
[2]J. N. Ospenson, *Acta Chem. Scand.* **4**, 1351 (1950)
[3]T. Urbanski, *Tetrahedron* **6**, 1 (1959)
[4]A. J. Sadlej and J. Dabrowski, *J. Mol. Structure* **7**, 1 (1971)
[5]H. Jensen and F. Rethwisch, *J. Amer. Chem. Soc.*, **50**, 1146 (1928)
[6]A. Coldberg and W. Kelly, *J. Chem. Soc.* 104 (1946)