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The influence of steric and polar effects on hydrogen bonding in 2-(N,N-diethylamino)-methyl-4-NO_2-phenols

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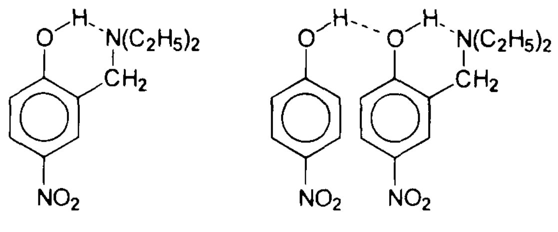
Two crystal structures consisting of 2-(N,N-diethylamino)-methyl-4-NO_2-phenol molecules were determined. In the triclinic crystals (with a = 9.527(2) Å, b = 11.268(3) Å, c = 11.408(3) Å, α = 87.80(3)°, β = 69.62(3)°, γ = 81.82(3)°, Z = 4, space group $P\bar{1}$) asymmetric cyclic dimers were found, formed by two nonequivalent $O^- \cdots H-N^+$ hydrogen bonds of 2.614(3) and 2.660(3) Å lengths. In the complex of 2-(N,N-diethylamino)-methyl-4-NO_2-phenol with 4-NO_2-phenol (orthorhombic crystals with a = 20.732(4) Å, b = 16.618(2) Å, c = 10.452(2) Å, Z = 8, space group $Pbca$) an intermolecular $O^- \cdots H-O$ (2.525(2) Å) hydrogen bond between 4-NO_2-phenol and zwitterionic 2-(N,N-diethylamino)-methyl-4-NO_2-phenol was found. In the latter molecule the intramolecular $O^- \cdots H-N^+$ (2.760(2) Å) bridge is formed. The zwitterionic molecules form chains along the crystallographic b axis by $NH^+ \cdots O$ (3.105(2) Å) hydrogen bridges. The $N-H^+$ groups participate in bifurcated hydrogen bonds. The influence of the steric strain caused by N-alkyl chains and polar interactions of the NO_2 group on the character of the hydrogen bond and the structure of cyclic dimers is discussed. The IR and UV spectra determined show the full agreement in description of the hydrogen bonding schemes, simultaneously demonstrating a drastic rearrangement of these schemes upon going to CCl_4 solutions.

KEY WORDS: Hydrogen bond; crystal structure; FT-IR spectra; 2-(N,N-diethylamino)-methyl-4-NO_2-phenol; cyclic dimers.

Introduction

The ortho-methylamino phenols are widely used as a model system of an intramolecular hydrogen bond. The crystal structures of a large group of such compounds have been determined and analyzed.[1] The ortho-Mannich bases (the products of Mannich condensation of secondary amines, formaldehyde and derivatives of phenol of ortho position) form nonplanar chelate rings, the structure of which is controlled by the strength of the hydrogen bond and steric repulsion of atoms forming the ring (cf. Scheme 1). It was found that the nonplanarity of this ring characterized by the N−C−C−C torsion angle correlates with the ΔpK_a ($= pK_a(BH^+) - pK_a(AH)$ in $A-H \cdots B$ bridge) as well as the $O(H) \cdots N$ distance and the C−O bond length. The intramolecular proton transfer, found even in non-



III. IV.

Scheme 1.

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polar solvents in a few compounds with the ΔpK_a values higher than 3, causes very serious structural changes.

Specific questions concerning the structure of compounds containing the 4-NO_2 substituent in the phenolic ring may arise. The first one concerns the influence of the NO_2 group on the proton transfer equilibrium position in the solid state. In 2-(N,N-dimethylamino)-methyl-4-NO_2-phenol (**I**) the zwitterionic structure in the solid state was observed,[2] despite the fact that the 2-(N,N-dimethylamino)-methyl-3,4,5-tri-Cl-phenol characterized by higher ΔpK_a values, forms a molecular hydrogen bond in the solid state. It was suggested[2] that this peculiarity results from a large polarization by the NO_2 group. The next determined structure of 4-NO_2-substituted Mannich base was for 2-(N,N-diisobutylamino)-methyl-4-NO_2-phenol (**II**).[3] In this case the screening of the hydrogen bridge by isobutyl groups reduces the polarization effect and intramolecular OH···N hydrogen bonds are formed. This shows that, besides the crystal packing forces, a combination of at least three molecular characteristics—ΔpK_a, polarization, and steric interactions determine the form of the hydrogen bond in the solid state. It was shown also that in solution, the position of the proton-transfer equilibrium can be found to be different from that in the solid state.[2] In solution, the regular shift of this equilibrium was found to correlate with

Table 1. Summary of data collection and processing parameters[a]

Formula	$C_{11}H_{16}N_2O_3$	$C_{11}H_{16}N_2O_3C_6H_5NO_3$
Colour	Yellow	Yellow
Molecular weight	224.26	363.37
Space group	$P\bar{1}$	*Pbca*
Temperature., °C	293(2) K	293(2) K
Crystal system	Triclinic	Orthorhombic
Cell constants		
a (Å)	9.527(2)	20.732(4)
b (Å)	11.268(2)	16.618(2)
c (Å)	11.408(2)	10.452(4)
α (deg)	87.80(3)	
β (deg)	69.62(3)	
γ (deg)	81.82(3)	
Cell volume (Å^3)	1136.2(4)	3601.3(11)
Formula units/unit cell	4	8
D_{cal}(mg × m^{-3})	1.311	1.340
μ_{cal}(cm^{-1})	0.960	8.63
Difractometer/scan	Kuma KM4/ω-2θ	
Radiation (A), graph monochromator	Mo$K\alpha$	Cu$K\alpha$
Max. crystal dimensions (mm)	0.35′0.35′0.40	0.20′0.20′0.25
Scan width (deg)	Variable	Variable
No. of stand. ref. and int.	3 (100 ref.)	3 (100 ref.)
Reflections measured	5416	3585
2θ range for data calc. (deg)	4.6 to 56.0 deg.	8.5 to 162.4 deg.
Range of *h*, *k*, *l*	0/12, −14/14, −13/15	−26/0, 0/21, 0/12
Reflections observed [$F_o > 4 \times \sigma(F_o)$]	3156	2538
Corrections applied	Lorentz and polarization effects	
Computer programs	Shelxs 86,[11] Shelxl 93[12]	
Soure of structure factors used	Programs	
Structure solution	Direct method	
Treatment of hydrogen atoms	Refined parameters: x, y, z, U_{iso}	
No. of parameters varied	417	320
weights[a] (a, b, f)	0.0663, 02294, 1/3	
GOF	1.088	1.138
$R_1 = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma(\lvert F_o\rvert)$	0.0406	0.0356
$wR_2 = \{\Sigma[wF_o^2 - F_o^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$	0.1086	0.1109
Function minimized	$\Sigma\, w(\Delta F^2)^2$	
Largest feature final diff. map(e × Å^{-3})	0.203 and −0.242	0.261 and −0.170

[a] $a_w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$ where $P = [f \times \text{Max. of } (0 \text{ or } F_o^2) + (1 - f) \times F_c^2]$.

the increasing length of N-chains[4] in 2-(N,N-dialkylamino)-methyl-4-NO$_2$-phenols. This is caused by the extension of the N-chain's shielding effect. An interesting question appeared to be the position of the proton transfer equilibrium in the solid state in the compound with two N-ethyl chains—in 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol (**III**), with intermediate steric effects between **I** and **II**. The structure of 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol is presented in this paper.

The second question concerns the conditions deciding whether intramolecular or intermolecular complexes are formed in the solid state. The working hypothesis was[2,5] that the molecular $O-H\cdots N$ systems form an intramolecular hydrogen bond and the ionic ones form intermolecular $N-H^+\cdots O^-$ hydrogen bridges arranged in cyclic dimers or chains.[1] Nevertheless, the evidence for the formation of the intramolecular hydrogen bonds of the ionic form was sought, because the assumption about the existence of such systems was a basis for interpretation of the hydrogen bonds polarity in low-polar solvents,[6] as well as interpretation of UV spectra[7] in systems characterized by ΔpK_a values below 3 units.[5] An increase of measured dipole moments with the solvent polarity[8] analogous to intermolecular complexes supports such an idea. It contradicts the alternative assumption about the cyclic dimers formation, which were detected for hydrogen bonds of ΔpK_a larger than 3, where a drastic decrease of measured dipole moments with concentration increase was stated. The existence of the ionic form of the intramolecular hydrogen bond in the complex of 4-NO$_2$-Mannich base with the 4-NO$_2$-phenol (**IV**) was demonstrated in this paper. Complex formation seems to be the supporting condition for such a structure, where formation of a strong hydrogen bridge $OH\cdots O^-$ type was discovered. It was known earlier,[9] that such complexes crystallize from the Mannich condensation reaction mixture in the case of 4-NO$_2$-phenol derivatives.

The third interesting question concerns the structure of cyclic dimers formed by polar systems. Commonly the low polarity, with nearly zero dipole moment value is expected for such complexes.[10] In the 2-(N,N-dimethylamino)-methyl-4-NO$_2$-phenol[2] such a structure with the symmetry center was found in the crystal, but in the case of a dimer of 2-(N,N-dimethylamino)-methyl-3,4,5,6-tetra-Cl-phenol,[3] two equivalent molecules related by the C_2 symmetry axis form a cyclic dimer by two identical $N^+-H\cdots O^-$ hydrogen bonds of 2.637(4) Å length (cf. Fig. 1).

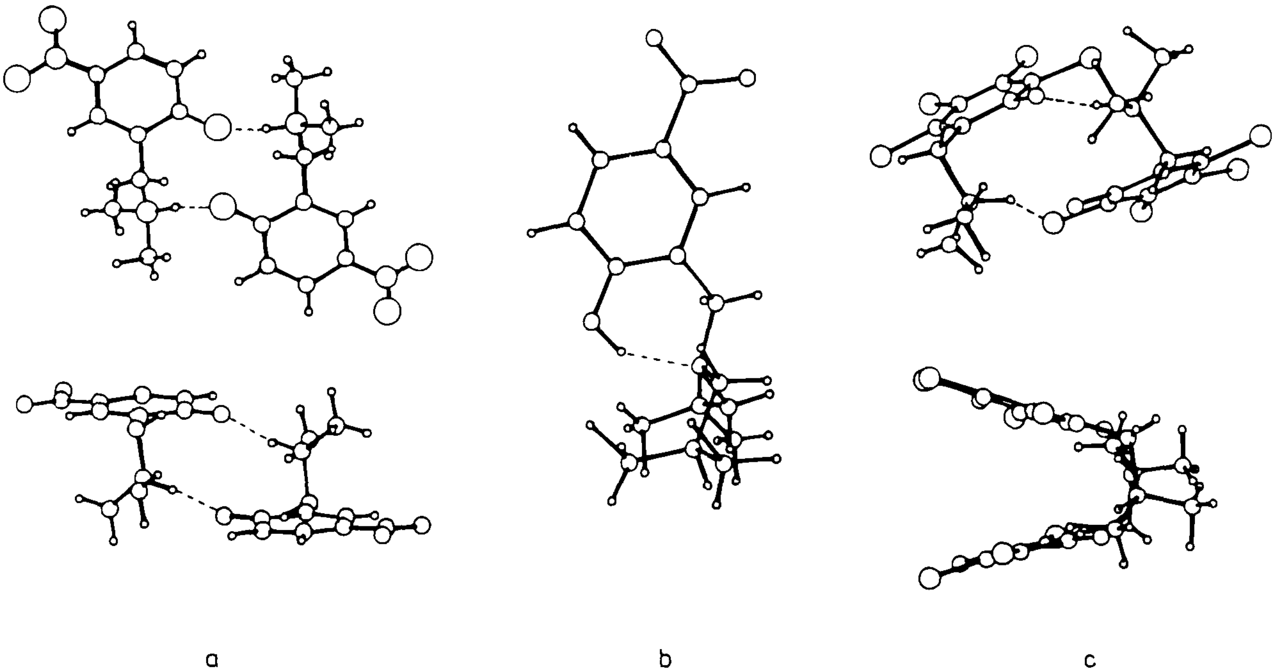


Fig. 1. The crystal structure of (a)—centrosymmetric dimer of 2-(N,N-dimethylamino)-methyl-4-NO$_2$-phenol (**I**),[2] (b)—intramoleculary hydrogen bonded the 2-(N,N-diisobutylamino)-methyl-4-NO$_2$-phenol (**II**),[3] (c)—cyclic dimer of 2-(N,N-dimethylamino)-methyl-2,3,4,5-tetra-Cl-phenol.[1,3]

Table 2. Final atomic coordinates and equivalent thermal parameters with esd's in parentheses for 2-(N,N-diethylamino)-methyl-4-NO_2-phenol (**III**)

	x/a	*y/b*	*z/c*	U_{eq}/U_{iso}
O11	0.1083(2)	0.1285(1)	0.8157(1)	0.0477(4)
O12	0.1761(3)	0.1367(2)	0.2555(2)	0.0940(7)
O13	0.4105(2)	0.1167(2)	0.2393(2)	0.0851(6)
N11	0.4070(2)	0.2620(2)	0.7252(2)	0.0382(4)
N12	0.2750(3)	0.1269(2)	0.3027(2)	0.0602(5)
C11	0.1442(2)	0.1312(2)	0.6972(2)	0.0387(4)
C12	0.2983(2)	0.1319(2)	0.1185(2)	0.0367(4)
C13	0.3392(2)	0.1293(2)	0.4910(2)	0.0415(4)
C14	0.2309(3)	0.1286(2)	0.4361(2)	0.0453(5)
C15	0.0804(3)	0.1321(2)	0.5086(2)	0.0562(6)
C16	0.0378(3)	0.1330(2)	0.6357(2)	0.0542(6)
C17	0.4108(2)	0.1370(2)	0.6813(2)	0.0413(4)
C18	0.4727(3)	0.2647(2)	0.8266(2)	0.0504(5)
C19	0.3643(3)	0.2362(3)	0.9513(2)	0.0602(6)
C110	0.4784(3)	0.3420(2)	0.6200(2)	0.0548(6)
C111	0.6465(4)	0.3127(4)	0.5614(4)	0.0875(11)
O21	0.1467(2)	0.3973(1)	0.8207(2)	0.0547(4)
O22	−0.4983(2)	0.5721(2)	0.8227(2)	0.0617(5)
O23	−0.3703(2)	0.6149(2)	0.6341(2)	0.0711(5)
N21	−0.1163(2)	0.2379(1)	1.0074(2)	0.0337(3)
N22	−0.3761(2)	0.5762(2)	0.7373(2)	0.0464(4)
C21	0.0269(2)	0.4366(2)	0.7987(2)	0.0396(4)
C22	−0.1181(2)	0.4303(2)	0.8928(2)	0.0353(4)
C23	−0.2474(2)	0.4788(2)	0.8719(2)	0.0355(4)
C24	−0.2404(2)	0.5317(2)	0.7587(2)	0.0387(4)
C25	−0.1015(3)	0.5385(2)	0.6650(2)	0.0493(5)
C26	0.0276(2)	0.4923(2)	0.6848(2)	0.0513(5)
C27	−0.1231(2)	0.3719(2)	1.0131(2)	0.0383(4)
C28	−0.0742(3)	0.1779(2)	1.1120(2)	0.0451(5)
C29	−0.1884(4)	0.2076(4)	1.2394(2)	0.0749(9)
C210	−0.2596(2)	0.2053(2)	0.9999(2)	0.0438(5)
C211	−0.2571(3)	0.0738(2)	0.9837(3)	0.0541(6)
H	0.300(3)	0.300(2)	0.760(2)	0.057(7)
H′	−0.042(2)	0.212(2)	0.935(2)	0.041(5)
H(1)	0.443(3)	0.132(2)	0.443(2)	0.050(6)
H(2)	0.009(3)	0.131(2)	0.471(3)	0.068(8)
H(3)	−0.062(3)	0.129(2)	0.686(3)	0.068(8)
H(4)	0.519(3)	0.112(2)	0.626(2)	0.048(6)
H(5)	0.388(2)	0.090(2)	0.755(2)	0.047(6)
H(6)	0.567(3)	0.208(3)	0.799(3)	0.073(8)
H(7)	0.499(3)	0.351(3)	0.832(3)	0.083(9)
H(8)	0.405(3)	0.243(3)	1.015(3)	0.079(9)
H(9)	0.354(5)	0.147(4)	0.941(4)	0.14(2)
H(10)	0.268(4)	0.292(3)	0.973(3)	0.087(9)
H(11)	0.450(3)	0.423(3)	0.655(2)	0.061(7)
H(12)	0.430(3)	0.336(2)	0.564(3)	0.071(8)
H(13)	0.697(5)	0.322(4)	0.628(4)	0.125(14)
H(14)	0.684(4)	0.366(4)	0.498(4)	0.122(13)
H(15)	0.678(4)	0.228(4)	0.533(3)	0.100(11)
H(16)	−0.340(2)	0.477(2)	0.935(2)	0.038(5)
H(17)	−0.098(3)	0.580(2)	0.590(2)	0.061(7)
H(18)	0.123(3)	0.500(2)	0.625(3)	0.070(8)
H(19)	−0.039(3)	0.387(2)	1.035(2)	0.047(6)
H(20)	−0.216(3)	0.400(2)	1.086(2)	0.048(6)
H(21)	−0.055(2)	0.094(2)	1.094(2)	0.046(6)
H(22)	0.015(3)	0.205(2)	1.106(2)	0.055(7)
H(23)	0.210(4)	0.292(3)	1.258(3)	0.095(11)
H(24)	−0.282(4)	0.174(3)	1.240(3)	0.114(13)
H(25)	−0.151(3)	0.167(3)	1.300(3)	0.087(9)
H(26)	−0.273(3)	0.249(2)	0.929(2)	0.061(7)
H(27)	−0.338(3)	0.235(2)	1.076(2)	0.058(7)
H(28)	−0.244(3)	0.031(3)	1.056(3)	0.070(8)
H(29)	−0.358(4)	0.060(3)	0.980(3)	0.086(9)
H(30)	−0.175(4)	0.041(3)	0.908(3)	0.080(9)

This demonstrates the possibility of the formation in solution of cyclic dimers with non-zero value of dipole moment. The structure of **III** gives an example of an even less symmetric cyclic dimer, where two different hydrogen bonds in a dimer were found.

Experimental

1. Synthesis of Mannich base from a stoichiometric mixture of 4-NO_2-phenol, formaldehyde and diethylamine in methanol was performed by a standard procedure.[9] After 6 hr of boiling the reaction mixture was cooled to give the yellow precipitate, which after recrystallization from water/methanol (50:50%) mixture (m.p. = 113.5°C) was studied by X-ray diffraction. It is further indicated as compound **IV**.

The filtrate, after all the routine steps of the Mannich synthesis[9] gave the yellow oil, which was crystallized from petroleum ether (m.p. = 74°C). It was indicated in this paper as compound **III**.

The IR spectra were recorded on NICOLET 205 FT-IR spectrophotometer with 2 cm^{-1} resolution in KBr pellets and in CCl_4 solutions with concentration $c \sim 0.005$ M/l.

The UV spectra were measured in n-hexane and ethanol solutions and in KBr pellets on CARY 1 VARIAN spectrophotometer with resolution 2 nm.

A summary of data collection is given in Table 1. Final atomic coordinates are given in Table 2 and Table 3. Anisotropic thermal parameters for non-H-atoms were applied.[13]

Results and discussion

The molecular structures and atom labeling systems are given in Fig. 2. Tables 4 and 5 present selected

Table 2b. Anisotropic displacement parameters (Å^2) for 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol (**III**)[a]

	U11	U22	U33	U23	U13	U12
O(11)	0.0477(8)	0.0562(9)	0.0324(7)	−0.0009(6)	−0.0061(6)	−0.0046(7)
O(12)	0.105(2)	0.141(2)	0.0542(11)	−0.0016(12)	−0.0484(12)	−0.0220(14)
O(13)	0.0823(14)	0.120(2)	0.0374(9)	−0.0036(10)	−0.0092(9)	0.0088(12)
N(11)	0.0328(8)	0.0506(10)	0.0323(8)	−0.0012(7)	−0.0134(6)	−0.0031(7)
N(12)	0.081(2)	0.0640(13)	0.0384(10)	−0.0005(9)	−0.0257(11)	−0.0069(11)
C(11)	0.0415(10)	0.0377(10)	0.0346(9)	−0.0018(8)	−0.0093(8)	−0.0071(8)
C(12)	0.0388(10)	0.0355(9)	0.0349(9)	0.0001(7)	−0.0115(8)	−0.0041(8)
C(13)	0.0436(11)	0.0406(10)	0.0359(10)	−0.0005(8)	−0.0086(8)	−0.0044(8)
C(14)	0.0569(13)	0.0466(11)	0.0348(10)	−0.0007(8)	−0.0179(9)	−0.0090(9)
C(15)	0.0568(14)	0.071(2)	0.0533(13)	0.0014(11)	−0.0304(11)	−0.0194(12)
C(16)	0.0419(12)	0.073(2)	0.0478(12)	−0.0005(11)	−0.0120(10)	−0.0181(11)
C(17)	0.0395(11)	0.0439(11)	0.0393(10)	0.0015(9)	−0.0145(8)	0.0002(8)
C(18)	0.0435(12)	0.070(2)	0.0433(12)	−0.0019(10)	−0.0226(9)	−0.0073(11)
C(19)	0.067(2)	0.077(2)	0.0403(12)	0.0031(12)	−0.0239(12)	−0.0091(14)
C(110)	0.0651(15)	0.0580(15)	0.0459(12)	0.0057(11)	−0.0205(11)	−0.0217(12)
C(111)	0.072(2)	0.102(3)	0.068(2)	−0.005(2)	0.011(2)	−0.035(2)
O(21)	0.0337(8)	0.0569(9)	0.0724(11)	−0.0110(8)	−0.0193(7)	0.0030(6)
O(22)	0.0382(8)	0.0720(11)	0.0684(11)	0.0092(9)	−0.0163(8)	0.0059(7)
O(23)	0.0792(12)	0.0790(12)	0.0623(11)	0.0257(9)	−0.0385(9)	−0.0052(9)
N(21)	0.0316(8)	0.0369(8)	0.0307(8)	0.0010(6)	−0.0103(6)	0.0002(6)
N(22)	0.0488(10)	0.0403(9)	0.0518(10)	0.0062(8)	−0.0222(8)	−0.0009(7)
C(21)	0.0332(10)	0.0356(10)	0.0491(11)	−0.0060(8)	−0.0124(8)	−0.0050(7)
C(22)	0.0355(9)	0.0322(9)	0.0383(9)	−0.0018(7)	−0.0129(8)	−0.0037(7)
C(23)	0.0327(9)	0.0331(9)	0.0369(10)	−0.0001(7)	−0.0075(8)	−0.0037(7)
C(24)	0.0390(10)	0.0351(10)	0.0413(10)	0.0032(8)	−0.0144(8)	−0.0021(8)
C(25)	0.0501(12)	0.0529(12)	0.0404(11)	0.0117(9)	−0.0102(9)	−0.0098(10)
C(26)	0.0379(11)	0.0582(13)	0.0485(12)	0.0056(10)	−0.0019(9)	−0.0119(10)
C(27)	0.403(10)	0.0386(10)	0.0388(10)	−0.0038(8)	−0.0183(9)	−0.0021(8)
C(28)	0.0443(12)	0.0538(13)	0.0372(10)	0.0062(9)	−0.0180(9)	0.0017(10)
C(29)	0.085(2)	0.092(2)	0.0344(13)	0.0087(13)	−0.0116(13)	0.006(2)
C(210)	0.0371(10)	0.0431(11)	0.0538(13)	0.0007(10)	−0.0197(10)	−0.0036(8)
C(211)	0.0549(14)	0.0451(12)	0.065(2)	0.0055(11)	−0.0227(12)	−0.0118(10)

[a] The anisotropic displacement factor exponent takes the form: $-2\,\pi^2\,[h^2\,a^{*2}\,U11 + \cdots + 2\,h\,k\,a^*\,b^*\,U12]$.

bond distances and valence angles. Selected torsional angles are presented in Table 6.

In the crystal structure 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol (**III**) forms cyclic dimers, R_2^2 (12),[14] lacking the symmetry center found earlier in the case of 2-(N,N-dimethylamino)-methyl-4-NO$_2$-phenol (**I**). The increase of the steric and shielding effects by extension of N-aliphatic chains from methyl to ethyl groups appears not to be sufficient to prevent an ionization, as was found in the case of diisobutyl derivative.[3] Two different bonds of $O^- \cdots H-N^+$ type can be characterized by the 2.614(3) and 2.660(3) Å of $O^-(H)-N^+$ distance, $H-N^+$ bonds length equal to 1.00(3) and 0.91(3) Å, the $H \cdots O^-$ distances equal to 1.65(2) and 1.78(2) Å as well as the $O-H \cdots N^+$ angles equal to 163(2) and 166(2) degrees. Nonlinearity of these $N-H^+ \cdots O$ bonds can be caused by attraction between H^+ and O^- atoms in neighbor hydrogen bonds, i.e., $H' \cdots O21$ (2.91 Å) and $H \cdots O11$ (2.75 Å).

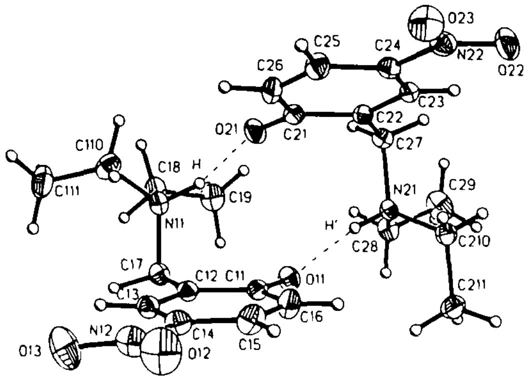
The packing scheme of two cyclic dimers in the crystal structure of **III** is shown in Fig. 3. The structure of **III** resembles the structure of the cyclic dimers in N,N-dimethyl derivative of tetra-Cl-phenol (cf. Fig. 1). The arrangement of atoms involved in the hydrogen bonding in **III** is, however, less symmetrical than in tetrachloro derivative, where two of $N^+-H \cdots O^-$ hydrogen bonds are equivalent.

The ionic or molecular form of the 4-NO$_2$-phenol in the solid state can be verified by the UV-Vis spectra, measured in KBr pellets. In **III** the maximum of the first long-wave absorption band is above 400 nm, which clearly indicates the ionic form of the hydrogen bond resembling the absorption of **III** in ethanol with the excess of KOH (with maximum at 410 nm) and

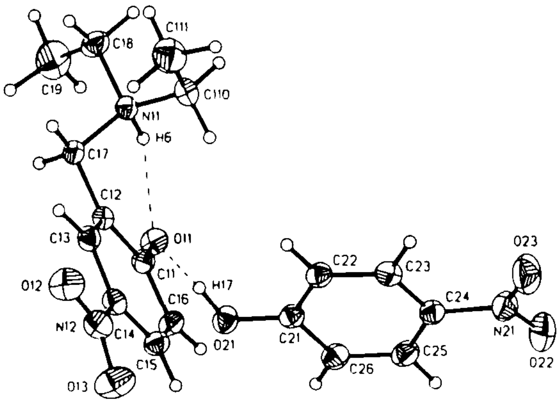
Table 3. Final atomic coordinates and equivalent thermal parameters with esd's in parentheses for complex of 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol with 4-NO$_2$-phenol (**IV**)

	x/a	*y/b*	*z/c*	U_{eq}/U_{iso}
O11	0.50304(4)	0.18213(5)	0.09263(11)	0.0448(3)
O12	0.44660(6)	−0.17479(6)	0.3241(2)	0.0680(4)
O13	0.35678(6)	−0.14206(7)	0.1444(2)	0.0814(5)
O21	0.42843(5)	0.28699(6)	−0.00054(11)	0.0481(3)
O22	0.23287(8)	0.49312(9)	0.3087(2)	0.0896(5)
O23	0.25566(8)	0.40318(11)	0.4515(2)	0.0871(5)
N11	0.59854(5)	0.14706(7)	0.26800(12)	0.0385(3)
N12	0.41113(6)	−0.12493(8)	0.18194(14)	0.0521(3)
N21	0.26067(6)	0.43127(9)	0.3433(2)	0.0605(4)
C11	0.47990(6)	0.11113(7)	0.11619(14)	0.0366(3)
C12	0.52121(6)	0.05048(7)	0.16758(13)	0.0358(3)
C13	0.49866(6)	−0.02619(7)	0.18947(15)	0.0396(3)
C14	0.43453(6)	−0.04461(8)	0.16302(15)	0.0405(3)
C15	0.39217(6)	0.01399(8)	0.1179(2)	0.0432(3)
C16	0.41416(6)	0.09054(8)	0.0963(2)	0.0418(3)
C17	0.59069(6)	0.07186(8)	0.1894(2)	0.0400(3)
C18	0.66846(7)	0.16785(10)	0.2849(2)	0.0546(4)
C19	0.69929(13)	0.1968(2)	0.1650(3)	0.0897(8)
C110	0.56153(8)	0.14580(10)	0.3920(2)	0.0510(4)
C111	0.57920(14)	0.0781(2)	0.4797(2)	0.0770(6)
C21	0.38778(6)	0.31878(7)	0.0840(2)	0.0391(3)
C22	0.38552(7)	0.29450(8)	0.2121(2)	0.0430(3)
C23	0.34249(7)	0.32974(9)	0.2953(2)	0.0453(3)
C24	0.30245(6)	0.39098(8)	0.2516(2)	0.0447(3)
C25	0.30313(7)	0.41556(9)	0.1266(2)	0.0497(4)
C26	0.34525(7)	0.37925(9)	0.0416(2)	0.0473(4)
H(1)	0.5278(8)	−0.0665(10)	0.220(2)	0.050(4)
H(2)	0.3468(8)	0.0027(9)	0.101(2)	0.042(4)
H(3)	0.3864(8)	0.1308(11)	0.072(2)	0.054(5)
H(4)	0.6125(8)	0.0316(11)	0.230(2)	0.053(5)
H(5)	0.6133(9)	0.0841(11)	0.109(2)	0.054(5)
H(6)	0.5769(10)	0.1863(12)	0.215(2)	0.070(6)
H(7)	0.6716(10)	0.2115(13)	0.355(2)	0.073(6)
H(8)	0.6889(11)	0.119(2)	0.323(2)	0.083(7)
H(9)	0.746(2)	0.211(2)	0.186(3)	0.118(9)
H(10)	0.702(2)	0.153(2)	0.091(4)	0.17(2)
H(11)	0.6746(14)	0.244(2)	0.125(3)	0.124(11)
H(12)	0.5150(10)	0.1411(11)	0.370(2)	0.069(5)
H(13)	0.5701(9)	0.2000(12)	0.434(2)	0.058(5)
H(14)	0.5519(14)	0.084(2)	0.564(3)	0.128(11)
H(15)	0.623(2)	0.085(2)	0.501(3)	0.112(10)
H(16)	0.571(2)	0.020(2)	0.436(3)	0.133(11)
H(17)	0.4571(13)	0.250(2)	0.038(3)	0.119(9)
H(18)	0.4179(8)	0.2549(10)	0.237(2)	0.051(4)
H(19)	0.3425(8)	0.3164(10)	0.389(2)	0.049(4)
H(20)	0.2730(10)	0.4574(13)	0.093(2)	0.070(5)
H(21)	0.3467(8)	0.3939(11)	−0.041(2)	0.051(5)

of **I** in the solid state. Double absorption of **IV** in the solid state indicates existence of both 4-NO$_2$-phenolate and 4-NO$_2$-phenol chromophores. The short-wave band resembles the absorption in n-hexane solution with maximum at 290 nm.



III



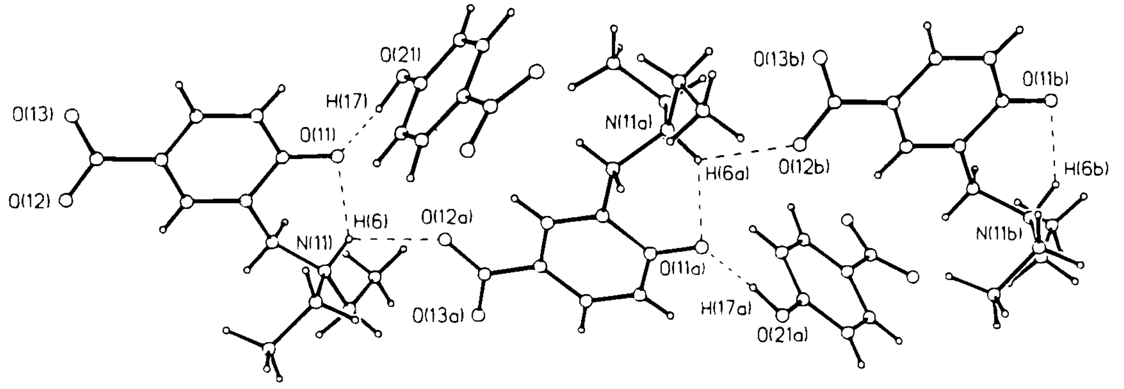
IV

Fig. 2. Molecular structure and atoms labelling system of 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol (**III**) and the complex of 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol with 4-NO$_2$-phenol (**IV**).

Existence of both these forms in **IV** is evident from the crystal structure (see Fig. 2b). The Mannich base part of the complex exists in the zwitterionic form, while 4-NO$_2$-phenol is molecular.

The arrangement of the hydrogen bonds is visualized in the Scheme 2.

The basic motif is a dimer between these subunits formed by a strong $O-H\cdots O^-$ (2.525 (2) Å) and nearly linear hydrogen bond (the $O-H\cdots O^-$ angle is equal to 174(1)°). In zwitterionic unit the intramolecular, ionic $N-H^+\cdots O^-$ hydrogen bond (S(6)—according the nomenclature of Etter[14]) is formed. The $N^+-H\cdots O^-$ distance is equal to 2.760(2) Å while the $N^+-H\cdots O^-$ angle is equal to 135(1)°. The N−C−C−C torsion angle, equal to 52.7(2)° is the highest of those observed in other ortho-Mannich



Scheme 2.

bases. Also a very long $O^-\cdots H(N^+)$ distance 2.00(3) Å is observed.

Some weakening of this hydrogen bond results probably from an engagement of the O^- acceptor in the another higher mentioned strong $O-H\cdots O^-$ bridge. The $N-H^+$ group on the other side forms bifurcated hydrogen bond, participating also in the $N-H^+$ O hydrogen bond (3.105 (2) A length, with $N-H^+\cdots O$ angle equal to 128(1)°) to the one of the oxygen atoms of NO$_2$ group of another Mannich base.

This hydrogen bonding arranges the dimers of the complex **IV** in chains (C(8) according)[14] nearly along the crystallographic *b* axis.

The IR spectra determined are in full accordance with the structural characteristics of the hydrogen bonding schemes in the solid state of both compounds

Table 3b. Anisotropic displacement parameters (A^2) for complex of 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol with 4-NO$_2$-phenol (**IV**)^a

	*U*11	*U*22	*U*33	*U*23	*U*13	*U*12
O(11)	0.0427(5)	0.0348(4)	0.0570(7)	0.0053(4)	−0.0052(4)	−0.0017(3)
O(12)	0.0804(8)	0.0390(5)	0.0845(10)	0.0113(6)	−0.0144(7)	−0.0064(5)
O(13)	0.0661(8)	0.0541(7)	0.1238(13)	0.0089(7)	−0.0195(8)	−0.0235(6)
O(21)	0.0479(5)	0.0500(5)	0.0464(7)	0.0060(5)	0.0034(5)	0.0088(4)
O(22)	0.0875(10)	0.0798(9)	0.1015(13)	−0.0215(8)	0.0068(8)	0.0354(8)
O(23)	0.0845(10)	0.1076(12)	0.0693(11)	−0.0057(9)	0.0242(8)	0.0141(8)
N(11)	0.0363(5)	0.0353(5)	0.0440(7)	−0.0046(5)	−0.0028(5)	0.0039(4)
N(12)	0.0588(7)	0.0398(6)	0.0578(9)	−0.0004(6)	−0.0005(6)	−0.0089(5)
N(21)	0.0430(6)	0.0641(8)	0.0743(12)	−0.0180(8)	0.0028(6)	0.0018(6)
C(11)	0.0374(6)	0.0342(6)	0.0382(8)	0.0002(5)	−0.0014(5)	0.0014(4)
C(12)	0.0338(5)	0.0364(6)	0.0372(8)	−0.0030(5)	−0.0005(5)	0.0030(4)
C(13)	0.0429(6)	0.0353(6)	0.0407(8)	−0.0016(5)	−0.0011(5)	0.0045(5)
C(14)	0.0451(6)	0.0340(6)	0.0423(9)	−0.0006(5)	0.0017(5)	−0.0033(5)
C(15)	0.0364(6)	0.0449(7)	0.0483(10)	−0.0003(6)	−0.0025(5)	−0.0018(5)
C(16)	0.0356(6)	0.0414(6)	0.0483(10)	0.0026(6)	−0.0045(5)	0.0032(5)
C(17)	0.0340(6)	0.0397(6)	0.0464(9)	−0.0086(6)	−0.0015(5)	0.0044(5)
C(18)	0.0385(7)	0.0485(7)	0.0768(13)	−0.0094(8)	−0.0078(7)	−0.0021(6)
C(19)	0.0694(13)	0.095(2)	0.105(2)	−0.016(2)	0.0241(13)	0.0351(13)
C(110)	0.0536(8)	0.0559(8)	0.0437(10)	−0.0108(7)	0.0027(7)	0.0047(6)
C(111)	0.090(2)	0.0862(15)	0.0552(14)	0.0116(11)	0.0025(12)	0.0042(12)
C(21)	0.0360(6)	0.0364(6)	0.0449(9)	0.0016(5)	−0.0027(5)	−0.0022(4)
C(22)	0.0427(6)	0.0409(6)	0.0454(10)	0.0030(6)	−0.0048(6)	0.0014(5)
C(23)	0.0458(7)	0.0488(7)	0.0412(10)	−0.0014(6)	−0.0027(6)	−0.0052(5)
C(24)	0.0348(6)	0.0458(7)	0.0535(10)	−0.0080(6)	−0.0012(6)	−0.0028(5)
C(25)	0.0421(7)	0.0458(7)	0.0611(11)	−0.0002(7)	−0.0076(7)	0.0061(5)
C(26)	0.0478(7)	0.0474(7)	0.0469(10)	0.0073(7)	−0.0046(6)	0.0052(6)

^{a} The anisotropic displacement factor exponent takes the form: $-2\pi^2\,[h^2 a^{*2}\,U11 + \cdots 2\,h\,k\,a^*\,b^*\,U12]$.

Table 4. Selected bond lengths (Å) and valence angles (°) with esd's in parentheses for 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol (**III**)

Lengths (Å)		Angles (°)	
O11–C11	1.274(2)	C110–N11–C18	110.9(2)
O12–N12	1.229(3)	C110–N11–C17	112.5(2)
O13–N12	1.232(3)	C18–N11–C17	113.1(2)
N11–C110	1.496(3)	O12–N12–O13	122.3(2)
N11–C18	1.498(3)	O12–N12–C14	118.8(2)
N11–C17	1.505(3)	O13–N12–C14	118.9(2)
N12–C14	1.430(3)	O11–C11–C16	123.2(2)
C11–C16	1.418(3)	O11–C11–C12	120.5(2)
C11–C12	1.430(3)	C16–C11–C12	116.3(2)
C12–C13	1.369(3)	C13–C12–C11	120.9(2)
C12–C17	1.489(3)	C13–C12–C17	121.9(2)
C13–C14	1.381(3)	C11–C12–C17	117.2(2)
C14–C15	1.379(3)	C12–C13–C14	120.2(2)
C15–C16	1.362(3)	C15–C14–C13	120.6(2)
C18–C19	1.493(3)	C15–C14–N12	119.7(2)
C110–C111	1.497(4)	C13–C14–N12	119.6(2)
O21–C21	1.268(2)	C16–C15–C14	120.0(2)
O22–N22	1.237(2)	C15–C16–C11	121.8(2)
O23–N22	1.225(2)	C12–C17–N11	111.8(2)
N21–C210	1.495(3)	C19–C18–N11	112.0(2)
N21–C28	1.496(2)	N11–C110–C111	114.6(3)
N21–C27	1.505(2)	C210–N21–C28	113.3(2)
N22–C24	1.417(3)	C210–N21–C27	110.7(2)
C21–C26	1.419(3)	C28–N21–C27	111.6(2)
C21–C22	1.433(3)	O23–N22–O22	121.4(2)
C22–C23	1.370(3)	O23–N22–C24	119.6(2)
C22–C27	1.488(3)	O22–N22–C24	119.0(2)
C23–C24	1.385(3)	O21–C21–C26	123.0(2)
C24–C25	1.391(3)	O21–C21–C22	120.2(2)
C25–C26	1.356(3)	C26–C21–C22	116.7(2)
C28–C29	1.497(3)	C23–C22–C21	120.3(2)
C210–C211	1.496(3)	C23–C22–C27	121.5(2)
		C21–C22–C27	118.2(2)
		C22–C23–C24	120.6(2)
		C23–C24–C25	120.6(2)
		C23–C24–N22	119.5(2)
		C25–C24–N22	119.9(2)
		C26–C25–C24	119.5(2)
		C25–C26–C21	122.3(2)
		C22–C27–N21	112.6(2)
		N21–C28–C29	114.4(2)
		N21–C210–C211	114.0(2)

Table 5. Bond lengths (Å) and angles (°) with esd's in parentheses in complex (**IV**) of 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol with 4-NO$_2$-phenol

Lengths (Å)		Angles (°)	
O11–C11	1.297(2)	C18–N11–C17	111.11(10)
O12–N12	1.235(2)	C18–N11–C110	113.19(13)
O13–N12	1.227(2)	C17–N11–C110	113.77(11)
O21–C21	1.331(2)	O13–N12–O12	122.18(13)
O22–N21	1.232(2)	O13–N12–C14	118.85(13)
O23–N21	1.228(2)	O12–N12–C14	118.97(12)
N11–C18	1.501(2)	O23–N21–O22	123.2(2)
N11–C17	1.504(2)	O23–N21–C24	118.8(2)
N11–C110	1.506(2)	O22–N21–C24	118.0(2)
N12–C14	1.434(2)	O11–C11–C16	123.10(11)
N21–C24	1.455(2)	O11–C11–C12	119.45(11)
C11–C16	1.421(2)	C16–C11–C12	117.43(11)
C11–C12	1.427(2)	C13–C12–C11	120.82(11)
C12–C13	1.376(2)	C13–C12–C17	121.31(11)
C12–C17	1.501(2)	C11–C12–C17	117.77(11)
C13–C14	1.392(2)	C12–C13–C14	119.66(12)
C14–C15	1.394(2)	C13–C14–C15	121.03(12)
C15–C16	1.370(2)	C13–C14–N12	120.02(12)
C18–C19	1.487(3)	C15–C14–N12	118.95(12)
C110–C111	1.496(3)	C16–C15–C14	119.67(12)
C21–C22	1.399(2)	C15–C16–C11	121.25(12)
C21–C26	1.408(2)	C12–C17–N11	112.56(10)
C22–C23	1.376(2)	C19–C18–N11	113.0(2)
C23–C24	1.391(2)	C111–C110–N11	114.4(2)
C24–C25	1.369(2)	O21–C21–C22	122.85(12)
C25–C26	1.384(2)	O21–C21–C26	118.08(14)
		C22–C21–C26	119.07(13)
		C23–C22–C21	120.23(13)
		C22–C23–C24	119.4(2)
		C25–C24–C23	121.73(14)
		C25–C24–N21	119.83(14)
		C23–C24–N21	118.4(2)
		C24–C25–C26	119.27(14)
		C25–C26–C21	120.3(2)

simultaneously showing a drastic rearrangement of these schemes on going to CCl_4 solutions.

In the solid state of the complex **IV** a broad absorption in a range of 3100–1700 cm^{-1} is observed, which should contain the absorption of $N^+-H\cdots O^-$ and $O-H\cdots O^-$ hydrogen bonds. The relatively intensive pick at 3080 cm^{-1} seems to correspond of $N-H^+\cdots O$ hydrogen bond absorption. Deuteration significantly decreases absorption in this region. Assuming a high limit of the isotopic spectroscopic ratio for the weakest $N^+-H\cdots Y^-$ type hydrogen bonds equal to 1.355[15] one can expect the intensity increase at about 2270 cm^{-1}. Some increase of the intensity in deuterated sample is really observed in this region (Fig. 4).

The lower frequency absorption seen in all the range between 2700 and 1700 cm^{-1} can be attributed to the $O-H\cdots O^-$ hydrogen bond of 2.525 Å length. The character of the absorption—two picks at about 2450 cm^{-1} and 1850 cm^{-1}—seems to be explained by the Fermi resonance.[16,17].

Deuteration leads to appearance of a single peak at ~ 1850 cm^{-1} in full accordance also with reference[15]

Table 6. Selcted torsion angles (°) for for 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol with 4-NO$_2$-phenol (**IV**) and 2-(N,N-diethylamino)-methyl-4-NO$_2$-phenol (**III**) with esd's in parentheses

Torsion angles	2-(N,N-dimethylamino)-methyl-4-NO$_2$-phenol (III)	Torsion angles	2-(N,N-dimethylamino)methyl)-4-NO$_2$-phenol with 4-NO$_2$-phenol (IV)
O11-C11-C12-C13	177.0(2)	O11-C11-C12-C13	−177.74(13)
C16-C11-C12-C13	−2.7(3)	C16-C11-C12-C13	3.8(2)
O11-C11-C12-C17	−3.7(3)	O11-C11-C12-C17	−1.3(2)
C16-C11-C12-C17	176.7(2)	C16-C11-C12-C17	−179.74(13)
C11-C12-C13-C14	1.5(3)	C11-C12-C13-C14	−1.0(2)
C17-C12-C13-C14	−177.8(2)	C17-C12-C13-C14	−177.32(14)
C12-C13-C14-C15	0.8(3)	C12-C13-C14-C15	−1.8(2)
C12-C13-C14-N12	179.5(2)	C12-C13-C14-N12	178.14(13)
O12-N12-C14-C15	4.8(3)	O13-N12-C14-C13	−171.7(2)
O13-N12-C14-C15	−175.8(2)	O12-N12-C14-C13	7.4(2)
O12-N12-C14-C13	−173.9(2)	O13-N12-C14-C15	8.2(2)
O13-N12-C14-C13	5.5(3)	O12-N12-C14-C15	−172.6(2)
C13-C14-C15-C16	−1.8(4)	C13-C14-C15-C16	1.5(2)
N12-C14-C15-C16	179.6(2)	N12-C14-C15-C16	−178.38(15)
C14-C15-C16-C11	0.4(4)	C14-C15-C16-C11	1.5(2)
O11-C11-C16-C15	−177.9(2)	O11-C11-C16-C15	177.54(14)
C12-C11-C16-C15	1.7(3)	C12-C11-C16-C15	−4.0(2)
C13-C12-C17-N11	100.5(2)	C13-C12-C17-N11	−130.82(14)
C11-C12-C17-N11	−78.8(2)	C11-C12-C17-N11	52.7(2)
C110-N11-C17-C12	−74.5(2)	C18-N11-C17-C12	−178.45(13)
C18-N11-C17-C12	158.8(2)	C110-N11-C17-C12	52.4(2)
C110-N11-C18-C19	153.5(2)	C17-N11-C18-C19	70.6(2)
C17-N11-C18-C19	−79.0(3)	C110-N11-C18-C19	−159.9(2)
C18-N11-C110-C111	57.9(3)	C18-N11-C110-C111	−69.1(2)
C17-N11-C110-C111	−70.0(3)	C17-N11-C110-C111	59.0(2)
O21-C21-C22-C23	176.3(2)	O21-C21-C22-C23	179.86(13)
C26-C21-C22-C23	−1.3(3)	C26-C21-C22-C23	−0.4(2)
O21-C21-C22-C27	−2.8(3)	C21-C22-C23-C24	−1.6(2)
C26-C21-C22-C27	179.7(2)	C22-C23-C24-C25	2.2(2)
C21-C22-C23-C24	1.6(3)	C22-C23-C24-N21	−175.65(12)
C27-C22-C23-C24	−179.3(2)	O23-N21-C24-C25	172.5(2)
C22-C23-C24-C25	−1.2(3)	O22-N21-C24-C25	−8.8(2)
C22-C23-C24-N22	177.1(2)	O23-N21-C24-C23	−9.7(2)
O23-N22-C24-C23	−174.6(2)	O22-N21-C24-C23	169.04(14)
O22-N22-C24-C23	3.5(3)	C23-C24-C25-C26	−0.8(2)
O23-N22-C24-C25	3.7(3)	N21-C24-C25-C26	177.02(13)
O22-N22-C24-C25	−178.2(2)	C24-C25-C26-C21	−1.2(2)
C23-C24-C25-C26	0.4(3)	O21-C21-C26-C25	−178.44(13)
N22-C24-C25-C26	−177.9(2)	C22-C21-C26-C25	1.8(2)
C24-C25-C26-C21	0.0(4)		
O21-C21-C26-C25	−177.0(2)		
C22-C21-C26-C25	0.5(3)		
C23-C22-C27-N21	96.0(2)		
C21-C22-C27-N21	−84.9(2)		
C210-N21-C27-C22	−70.2(2)		
C28-N21-C27-C22	162.6(2)		
C210-N21-C28-C29	−60.7(3)		
C27-N21-C28-C29	65.1(3)		
C28-N21-C210-C211	−58.3(3)		
C27-N21-C210-C211	175.4(2)		

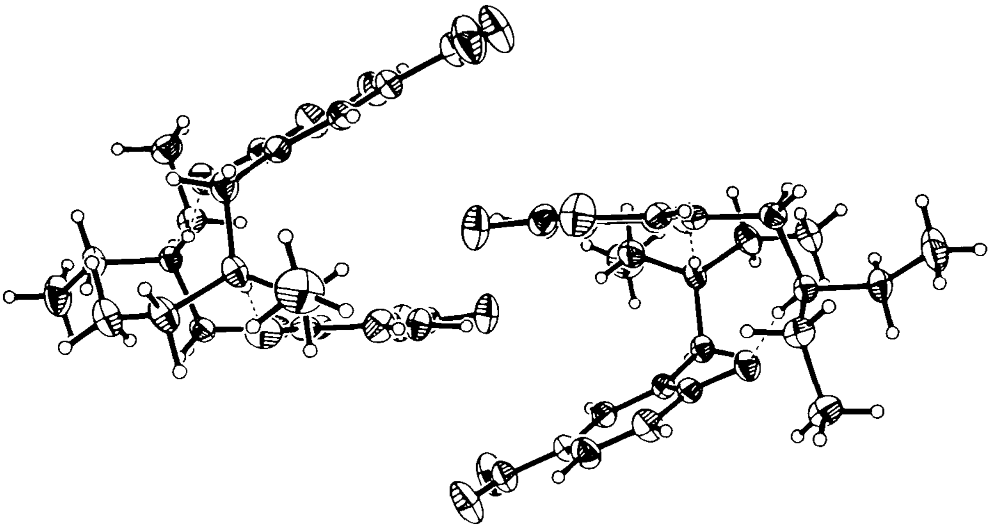


Fig. 3. The arrangement of cyclic dimers of **III** in the crystal structure.

where the Fermi resonance was not observed for ν(OD) absorption.[16] Some weakening of the $O-H\cdots O^-$ hydrogen bond in our case can be mentioned in comparison to hydrogen bonding in N,N,N',N'-tetra amyl-1,2-diammonium-ethane di[hydrogen-(bis pentachlorophenolate)][18] One can attribute this effect to the competition of the $N^+-H\cdots O^-$ and $O-H\cdots O^-$ hydrogen bonds to the same oxygen atom acceptor. On the other hand an increase of the absorption below 1700 cm^{-1} can not be completely precluded. The absorption of the $O-H\cdots O^-$ hydrogen bond in this region can be suggested from some absorption increase within 1000–400 cm^{-1} range upon cooling to liquid nitrogen temperatures.

Interesting changes in the IR spectra of **IV** are observed when changing to nonpolar solvent solutions (Fig. 5). The band with the maximum at about 2630 cm^{-1} suggests formation of the intramolecular $O-H\cdots N$ hydrogen bond in solution like in Mannich base **I**.[2,19] The most spectacular, however, is the appearance of the absorption of free 4-NO_2-phenol at ~3595 cm^{-1}. The intermolecular complexes are bro-

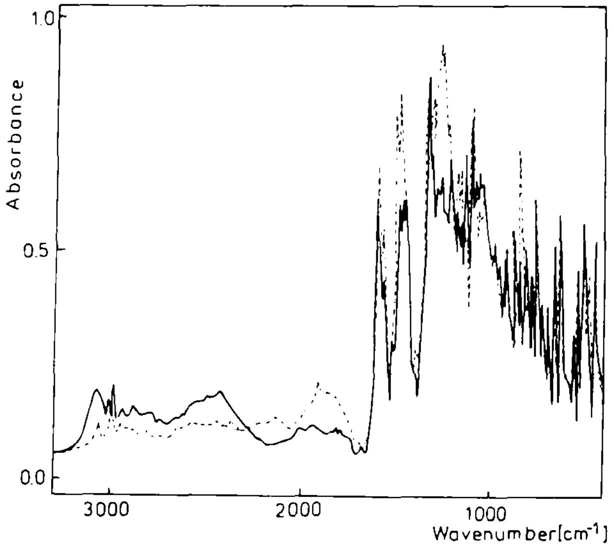


Fig. 4. IR spectra of **IV** in KBr pellets: full line—nondeuterated sample, dashed line—OH deuterated sample.

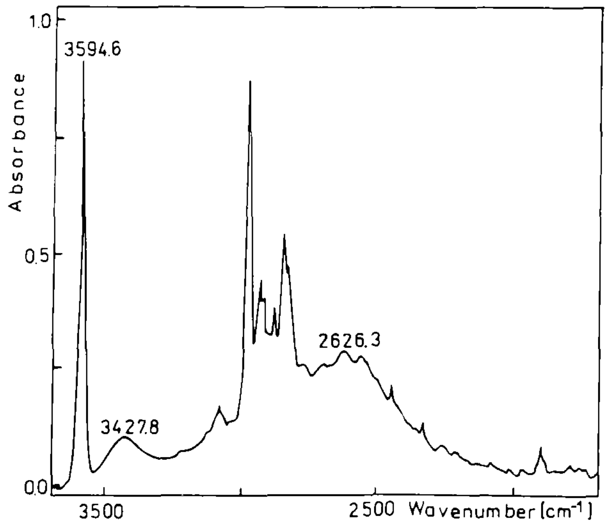


Fig. 5. IR spectrum of **IV** dissolved in CCl_4, $c=0.005$ M/dm^3, $d=9.55$ mm.

ken in the solutions. This is caused by the change of the character of intramolecular hydrogen bonding.

Neutral oxygen atom in such intramolecular hydrogen bond appears to be much less attractive proton acceptor for 4-NO$_2$-phenol molecule in solution, than the negatively charged oxygen atom in the solid state. Nevertheless one can assign the absorption band at 3428 cm^{-1} to the associated 4-NO$_2$-phenol molecules. Separate studies of 4-NO$_2$-phenol spectra as a function of concentration in CCl$_4$ solutions show that self-association leads to the absorption peak at 3452 cm^{-1} (for comparison 3327.5 cm^{-1} in the solid state). This suggests that the absorption observed in Fig. 5 is connected with complexation of 4-NO$_2$-phenol with Mannich base. The position of this band in comparison with the $O-H\cdots O^-$ absorption in the solid state demonstrates how drastically is lowered the $O-H\cdots O$ hydrogen bond strength in solution.

The IR spectrum of **III** in KBr (Fig. 6) resembles the ionic $N^+-H\cdots O^-$ spectrum of **I** in the solid state. The broad absorption resulting from two hydrogen bonds (cf. Table 8.) can be characterized by the position of the band's center of gravity located at 2360 cm^{-1} (2280 cm^{-1} in **I**).

Figure 7 shows the spectrum of Mannich base **III** in solution. The absorption at 2627 cm^{-1} suggests formation of intramolecular $O-H\cdots N$ hydrogen bond. The assignment is supported by the spectrum of the OD deuterated form. The spectroscopic isotopic ratio (SIR) calculated for the most pronounced peaks of nondeuterated and deuterated samples is 1.30. Analogous features of the IR absorption in the solid state and in nonpolar solvents of **I** were shown earlier.[2] Calculated SIR in **I** was 1.32 in accordance with the longer $O\cdots H-N^+$ distance (cf. Table 8).

The structural characteristics of four different compounds of 2-(N,N-dialkylamino)-methyl-4-NO$_2$-phenol are presented in Table 7. The details of hydrogen bond structures for all these compounds are given in Table 8.

Comparison of the structure parameters for different 4-NO$_2$-phenol Mannich bases allows one to distinguish the molecular and ionic structures of 4-NO$_2$-phenol subunit. In **I**, **III**, and **IV**, the C–O(H) distances are short 1.274–1.297 Å. In molecular 4-NO$_2$-phenol units, the C–O 1.341 Å and 1.332 Å lengths were found in **II** and **IV**, respectively, which are characteristic of strongly interacting phenols.

In the ionic subunits the p-quinonoid structures participate in the ground state structure description. The C–C bonds with C11 atom participation are within 1.420–1.430 Å limits. The C–C bonds parallel to the long axis of 4-NO$_2$-phenolate are substantially shortened (from 1.376 Å to 1.356 Å). The C–C bonds with the C4 atom participation are usually less sensitive for such effects.

The C–C bond between the methylene group and the C12 atom is the longest in the molecular form (1.513(3) Å, when in the ionic forms it is within the range 1.489(3)–1.501(2) Å). The C–N bonds between the methylene C atom and the amine group are longer in the ionic forms (within 1.505(2)–1.511(2) Å limits) than in the molecular one (1.488(3) Å). The distances

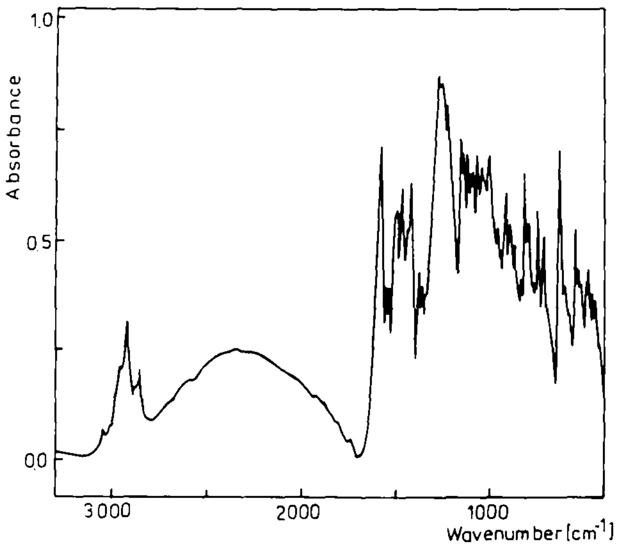


Fig. 6. IR spectrum of **III** in KBr pellets.

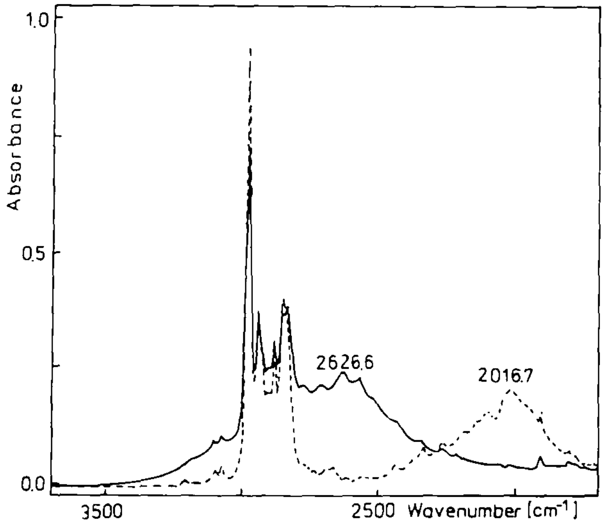


Fig. 7. IR absorption spectra of **III** dissolved in CCl$_4$; full line—nondeuterated sample, dashed line—OH deuterated sample.

Table 7. Comparison of selected bond lengths (Å) in four structures consisting the 4-NO$_2$-2-(N,N-dialkylmethyl) phenol subunit[a]

Atoms	(I)[2]	(II)[b]	(III)		(IV)	
O11−C11	1.283(3)	1.343(3)	1.274(2)	1.268(2)	1.297(2)	1.331(2)
C11−C12	1.433(3)	1.415(4)	1.430(3)	1.433(3)	1.427(2)	1.399(3)
C12−C13	1.373(3)	1.382(3)	1.369(3)	1.370(3)	1.376(2)	1.376(2)
C13−C14	1.390(3)	1.389(4)	1.381(3)	1.385(3)	1.392(2)	1.391(2)
C14−C15	1.395(3)	1.381(4)	1.379(3)	1.391(3)	1.394(2)	1.369(2)
C15−C16	1.365(3)	1.383(4)	1.362(3)	1.356(3)	1.370(2)	1.384(2)
C16−C11	1.428(3)	1.388(4)	1.418(3)	1.419(3)	1.421(2)	1.408(2)
C14−N12	1.425(3)	1.461(3)	1.430(3)	1.417(3)	1.434(2)	1.455(2)
N12−O12	1.229(3)	1.229(3)	1.229(3)	1.237(2)	1.235(2)	1.232(2)
N12−O13	1.234(3)	1.224(4)	1.232(3)	1.225(2)	1.227(2)	1.228(2)
C12−C17	1.491(3)	1.513(3)	1.489(3)	1.488(3)	1.501(2)	—
C17−N11	1.511(2)	1.488(3)	1.505(3)	1.505(2)	1.504(2)	—
C12−C11−C16	116.6(2)	120.3(2)	116.3(2)	116.7(2)	117.43(11)	119.07(13)
O12−N12−O13	121.4(2)	123.1(3)	122.3(2)	121.4(2)	122.18(13)	123.2(2)

[a] Atoms numbering like in Fig. 2.

[b] T. Glowiak, A. Koll, results not published, cf.[1]

between the nitrogen atoms of nitro groups and C14 atom are within the range 1.417(3)–1.434(2) Å in 4-NO$_2$-phenolate subunits, while in 4-NO$_2$-phenol moieties 1.461(3) Å and 1.452(2) Å values were found.

All the phenyl rings C12−C11−C16 angles are strongly reduced from 120° in the ionic forms (by 2.5–3.7°) while in the molecular forms these angles are 120.3(2)° and 119.1(2)° (in **II** and **IV**, respectively). The O−N−O angles in NO$_2$ groups are 123.1(3)° in molecular forms and 121.8 ± 0.7° in the 4-NO$_2$-phenolates in **I**, **III**, and **IV**.

Table 8 presents the parameters for the hydrogen bonds in four ortho-Mannich bases formed by derivatives of 4-NO$_2$-phenol, which differ only in the length of the N-aliphatic chains. Tables 7 and 8 demonstrate, that the length of the N-chains strongly influences the scheme of hydrogen bonds. For shorter chains (N,N-dimethyl and N,N-diethyl) derivatives the cyclic dimers are formed. In molecule **I** it is a fully centrosymmmetric unit, while in **III**, the cyclic dimer appears to be asymmetric; two different hydrogen bonds are formed. In addition, some of the parameters describing the phenyl rings are significantly (more than 3 σ) different. This effect probably results also from different crystal packing conditions.

Conclusion

The ortho-methylamino phenols can form molecular O−H···N or zwitterionic O^{-}···H−N^{+} hydrogen bonds. In compounds with −NO$_2$ substituent the zwitterionic forms are more easily formed than in compounds with fewer polar substituents. This results from strong polarization influence of -NO$_2$ group.

Table 8. Hydrogen bond length (Å) and angles (°) with esd's in parentheses

Compound	D−H···A	D−H	D···A	H···A	<D−H···A	**Ref.**
I	O ···H−N^{+}	0.97(2)	2.667(2)	1.71(2)	169(2)	2
II	O···H−N	1.03(9)	2.62(9)	1.65(9)	156(7)	3
III	O ···H−N^{+}	0.99(2)	2.614(3)	1.65(2)	163(2)	This work
	O ···H−N^{+}	0.90(2)	2.660(3)	1.78(2)	166(2)	
IV	O ···H−O	0.94(3)	2.525(2)	1.59(3)	174(1)	This work
	O ···H−N^{+}	0.97(2)	2.760(2)	2.00(3)	135(1)	
	O···H−N	0.97(2)	3.105(2)	2.42(3)	128(1)	

In this paper the strong influence of steric effects on the character of the hydrogen bond in crystal structures consisting of the 2-(N,N-dialkylamino)-methyl-4-NO_2-phenol moiety was demonstrated. The systems with short (methyl and ethyl) N-chains form zwitterionic cyclic dimers while the isobutyl groups[1,3] are sufficiently bulky to prevent the polarization effects of neighboring molecular dipole moments.

In the two structures presented here, the participation of 2-(N,N-diethylaminomethyl)-4-NO_2-phenol is different from the point of view of the character of hydrogen bonds formed. In the structure of pure Mannich base **III**, a cyclic dimer between two zwitterionic molecules ($R_2^2(12)$) was found, resembling the structure of 2-(N,N-dimethylamino)-methyl-2,3,4,5-tetra-Cl-phenol. This feature demonstrates that the different forms of cyclic dimers can exist and the polarity of such units found in the solution is not unusual.

In the case of the complex of Mannich base with 4-NO_2-phenol **IV** the ionic structure of the intramolecular hydrogen bond S(6) was found. This hydrogen bond appears to be rather weak with $O \cdots N^+$ distance of 2.760(2) Å in comparison to intramolecular systems studied thus far. The $O \cdots H$ distance is long (2.00(3) Å). This hydrogen bond is also strongly bent; the $N^+-H \cdots O$ angle is equal to 136(1)°. This $N-H^+$ donor participates in bifurcated hydrogen bond. The second hydrogen bridge $N-H^+ \cdots O$ (3.105(3) Å) is formed to one of the oxygen atoms of 4-NO_2 group, another molecule of Mannich base. Those $N-H^+ \cdots O$ hydrogen bonds form chains (C(8)) along the crystallographic *b* axis. Very strong hydrogen of the $O^- \; H-O$ type ($O \; O$ distance is equal to 2.525(2) Å) was found between the phenol and phenolate units. This bond is almost linear (the $O \cdots H-O$ angle equals to 174(1)°). The existence of this hydrogen bond probably weakens the intramolecular interaction in the $O^- \cdots H-N^+$ bond. The spectroscopic (UV and IR) characteristics of the hydrogen bond are in accordance with the structures discussed above. The strong influence of solvent on the form of the hydrogen bonds in studied systems was demonstrated.

Supplementary material. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5252 and CCDC-1003/5291. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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