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# A STUDY OF THE DONOR PROPERTIES OF THE CARBONYL GROUP OF PYRIDONES

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**Abstract**—The donor properties of the C=O group of pyridones have been examined by studying the IR spectra of their complexes with mercury-(II)-chloride and with hydroquinone. The complexes with mercury chloride are formed by a weak O···Hg donor-acceptor bond, while the others have the character of strongly H-bonded salts of hydroxypyridinium cations. The dipole moment of N-methyl-3-pyridone, not reported so far, has also been measured, (7·2 D). These results, and the agreement between the theoretical and the experimental dipole moments, support the prediction that the donor properties of the C=O group are very similar for the three isomers.

In a previous theoretical paper on the $\pi$-electronic structure of pyridones[1] we gave an approximate quantitative basis to the relationship between the different isomers and showed that the amide form of 3-hydroxypyridine could exist. This prediction was substantiated by the isolation and characterization of N-methyl-3-pyridone (2). The representation of the pyridone isomers was investigated[2] by a M.O-localization calculation and it was found that the classic formulae adequately represent the $\pi$-electron localization in the pyridone system.

Our results also suggest that the three isomers are rather similar, a conclusion which has been confirmed by a calculation by Benson and Murrell.[3] A more recent all-valence-electron CNDO calculation has shown that the CO group of the pyridone is strongly polarized:[4] its O atom in all the isomers bears a negative charge of about 0·5*e*, nearly 95% localized on the 2p$\pi$ atomic orbital, and its C atom has the largest electronic vacancy in the molecule (+0·32 to +0·41) which is 70 to 50% localized in the 2p$\pi$ orbital. The dipole moments based on this charge distribution were in quite good agreement with those observed for N-methyl-2- and N-methyl-4-pyridone. We have now measured the dipole moment for N-methyl-3-pyridone, 7·2 ± 0·5 D at 25°, which also agrees with the predicted value.

In order to test our conclusions further and to help clarify, with a more systematic search, some aspects of the donor properties of the CO group of pyridones we have examined their behaviour in the formation of addition compounds. Mercury-(II)-chloride was chosen as a moderately weak acceptor known[5] to produce only minor alterations in the structure of the donor molecule. Hydroquinone was chosen as the acid acceptor, in the hope of obtaining crystalline salts which would allow us to more easily identify the nature of the donor-acceptor bond. Complexes of some pyridones with both acceptors have been prepared previously. The mercury(II)-chloride complex with 1-methyl-2-pyridone (1) has been studied in some detail,[6] but that with 1-methyl-4-pyridone(3) was only incidentally mentioned[7] in synthetic work about fifty years ago. The hydroquinone salt of 1-methyl-2-pyridone has been reported[8] together with other "unusual pyridone salts" of pentacyanopropene.[9] Other "unusual... complexes" have been obtained[6,10] from the iodomethylates of hydroxypyridines. They have the stoichiometry of salts of N-methylpyridones with hydrogen iodide and the structure of their donor-acceptor bond awaits further study.

### *Complexes with mercury(II)-chloride*

The formation of 1:1 adducts is possible in all cases; adducts of different, well defined, compositions are also formed with some pyridones. The precautions necessary for avoiding contamination of each one by the others are detailed in the Experimental.

The IR spectra in the C=O group stretching region were used to study the nature of the donor-acceptor bond. The basis of our comparison has been the spectrum of the free base using the assignments which Coburn and Dudek[11] have deduced from the $^{18}O$ isotopic band shift for the 2- and 4-*oxo* isomers, and the assignment we have previously discussed[1] for the 3-*oxo* compound.

The latter assignment agrees with the one we now propose for 1,6-dimethyl-3-pyridone, (4), described here for the first time. Data are given in Table 1.

Table 1. Carbonyl IR absorption bands (cm$^{-1}$) of 1:1 adducts of N-methyl-pyridones with HgCl$_2$

| | Base[a] | Adduct | Shift |
|---|---|---|---|
| 1-Methyl-2-pyridone (1) | 1583 | 1560 | 23 |
| | 1659 | 1652 | 7 |
| | | 1648 | 11 |
| 1-Methyl-3-pyridone (2) | 1512 | 1493 | 19 |
| | | 1500 | 12 |
| | 1590 | 1560 | 30 |
| | | 1570 | 20 |
| 1-Methyl-4-pyridone (3) | 1401 | 1360 | 41 |
| | | 1370 | 31 |
| | 1575 | 1510 | 65 |
| | | 1522 | 53 |
| 1,6-Dimethyl-3-pyridone (4) | 1525 | 1512 | 13 |

[a]Spectra and assignments as in Refs 1 and 11.

The small frequency shift of the CO group vibrational modes indicates that the complex formation involves the C=O group as donor and the Hg atom as acceptor, as it parallels the behaviour previously reported[5] for adducts of the same type. The band shift of the 4-*oxo* isomer complex is much larger than that of the others and should correspond to the strongest donor-acceptor bond in the series.

The spectra of the complexes with ratios different from 1:1 show the same features, but cannot be compared on the same basis as the others. Their more detailed analysis is beyond the scope of present paper.

*Complexes with hydroquinone*

The adduct of **1**, already known,[9] has a 2:1 ratio of base to hydroquinone. We have now obtained 1:1 adducts with **2** and **3**, and two different adducts, having 1:2 and 2:1 ratios, with the compound **4**.

We have limited ourselves to the evidence obtainable from the IR spectra of the solids in the $3\mu$ region, since the complexity of the $5$–$7\mu$ region makes an analysis of the CO group absorption meaningless. The results are listed in Table 2.

Table 2. H-bond absorption bands (cm$^{-1}$) of adducts[a] of N-methyl-pyridones with hydroquinone (Hy)

| Base | Adduct stoichiometry | Bands |
|---|---|---|
| 1-Methyl-2-pyridone (1) | 2(1)·(Hy) | 2590; 2610<br>2700 |
| 1-Methyl-3-pyridone (2) | (2)·(Hy) | 2590; 2700 |
| 1-Methyl-4-pyridone (3) | (3)·(Hy) | 2750 |
| 1,6-Dimethyl-3-pyridone (4) | (4)·2(Hy) | 3300; 2620; 2700; 2750 |
| 1,6-Dimethyl-3-pyridone (4) | 2(4)·(Hy) | 2700;<br>broad, max. from 2250 to 2540.<br>broad, max. from 1830 to 1840. |

[a]Bands in the 3000–3100 region, which almost overlap those present in the starting compounds, are assigned to the C—H vibrations and not tabulated.

The spectra of the 1:1 adducts of **2** and **3** and of the 2:1 adduct of **1** are very similar. The prominent maxima resemble those found in the crystal spectra of the acid salts of carboxylic and other acids[12–14] and suggest a strong O—H···O H-bond with the second oxygen possessing a marked anionic character. The 1:1 adducts must have a structure where the OH groups of hydroquinone are also strongly H-bonded; this is possible if a self-association of the quinhydrone type is present in the lattice, e.g. as in **5** and **6**. Of the various structures proposed for the 2:1 adduct of **1** by Thyagarajan *et al.*[9] the models **7** or **8** seem in best agreement with the observed spectra.

The 1:2 adduct of **4** has a sharp strong band at 3300 cm$^{-1}$, which should be assigned as a $\nu_{OH}$ of hydroquinone.[15] The absorption in the 2600–3000 cm$^{-1}$ region is very similar to that of the 1:1 adducts. A structure model for this compound must therefore show H-bonds like those found in the hydroquinone crystals[15] and in **5**. A possible structure of this kind is **9**.

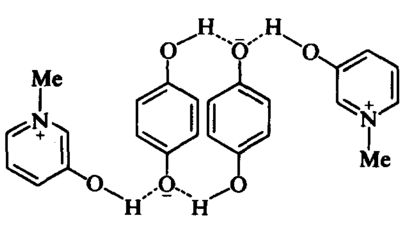
The IR absorption of the 2:1 adduct of **4** is very similar to the spectra reported by Hadzi[16] as typical of very strong O—H···O bonds. In order to interpret these results we have prepared the deuterated complex and recorded its spectrum (Fig 1). This shows a broad band with a maximum at 1910 cm$^{-1}$ and a new band at 1498 cm$^{-1}$ of about the same intensity as the neighbouring bands common to the H- and D-complexes. The H/D frequency ratio (1840/1498) = 1·23 and (2450/1910) = 1·28 show that this adduct is one of the few H-bonded salts where both bands are consistently displaced by deuteration.

According to literature reports[12–14,16] these features suggest the presence in the crystal lattice of very strong H-bonds with O···O distance less than 2·6 Å.

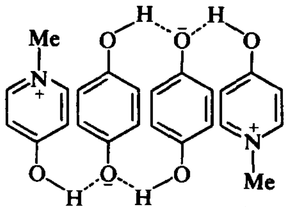
## CONCLUSIONS

The donor-acceptor bond of the mercury(II)-chloride adducts is fairly weak: the shift of the CO absorption band is comparable to that found with the adducts of aldehydes and ketones[5] and can be interpreted in the same way.[17]

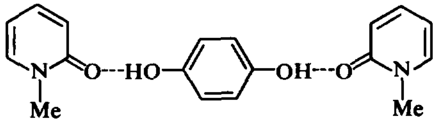
The common character of the hydroquinone adducts is the formation of 1-methyl-hydroxy-



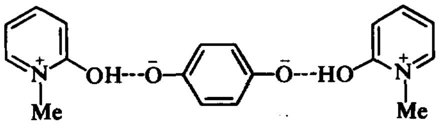
**5**



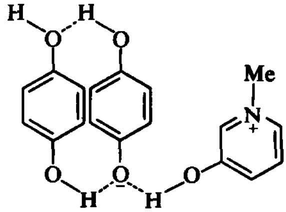
**6**



**7**



**8**



**9**

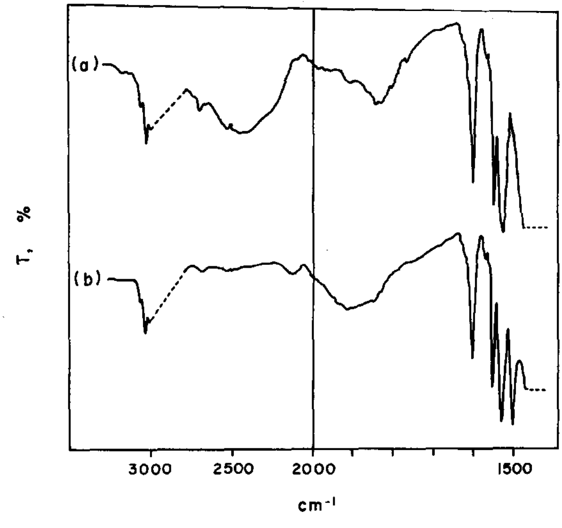


Fig 1. Spectra of the 2:1 complex of 1,6-dimethyl-3-pyridone with hydroquinone: *a* normal; *b* deuterated. (Nujol band in the dashed region).

pyridinium cations which become H-bonded to the anions of hydroquinone in a variety of ways.

In conclusion, the donor properties of the CO group of the three pyridone isomers appear to be similar, and we believe there are no grounds for considering as distinct or peculiar the properties of the 3-*oxo* isomers, ($\beta$-pyridones), or the analogous *oxo*-tautomers of the hydroxy-aza-aromatic series[20] in this respect. This conclusion is in agreement with the calculated[4] ground state charge distribution and dipole moments, and therefore supports the interpretation we have proposed previously[1,2] for the electronic structure of these molecules.

## EXPERIMENTAL

*Materials.* N-methyl-pyridones were prepared as reported in refs. 1 and 6.

1,6-*Dimethyl*-3-*pyridone*. Commercial 6-methyl-3-hydroxypyridine (9 mmoles) and (12·7 mmoles) MeI were dissolved in acetone (4 ml) in a sealed steel cylinder and were maintained at 100° for 4 hr. The solid methiodide was washed with acetone and crystallized from EtOH-ether, m.p. 248° (dec). The salt was treated with a suspension of $Ag_2O$ in water, the filtered soln dried at reduced pressure, the residue dissolved in MeOH and ether added. A white ppt was crystallized from acetone, m.p. 70°. (Found: C, 47·35; H, 8·64; N, 8·01. Calc. for $(C_7H_9NO)\cdot 3H_2O$: C, 47·44; H, 8·53; N, 7·91%). Spontaneous loss of water and dehydration at reduced pressure gave m.p. 144–148°. (Found: C, 63·73; H, 7·59; N, 10·80. Calc. for $(C_7H_9NO)\cdot\frac{1}{2}H_2O$: C, 63·62; H, 7·63; N, 10·80%).

Commercial hydroquinone was crystallized from dioxan. The CIBA sublimated mercury(II)-chloride was used without further purification.

The m.ps (uncorrected) were determined using either a Koffler or Buchi apparatus. The dipole moment of 1-methyl-3-pyridone is reported in Table 3. The IR spectra were recorded as nujol or fluorolube mulls with a Perkin-Elmer mod. 125 prism-grating spectrophotometer. The PMR spectra were used in addition to elemental analysis for determining the *donor*:*acceptor* ratio of the complexes, and were recorded with a Varian HA-100 instrument. The procedure described in Ref 8 was used for the hydroquinone complexes and the procedure described by Ward[18] was adopted for the mercury-chloride complexes. The solvent was DMSO, with TMS as the internal standard. The peak intensity was calibrated by adding known amounts of 1,3,5-trimethoxy-*s*-triazine, $\delta = 3{\cdot}90$ ppm to the soln. Microanalyses were carried out in the Micro-analysis Laboratory of the Istituto Superiore di Sanità.

### *Mercury(II)-chloride complexes*

(a) *With* 1-*methyl*-2-*pyridone*. Prepared as described in Ref 6 and crystallized from acetone, m.p. 127°. An identical product was obtained from an aqueous soln, as described by von Pechmann.[19]

(b) *With* 1-*methyl*-3-*pyridone*. A few drops of an acetone soln of mercury(II)-chloride were added to a soln of the base in the same solvent. The yellow ppt was filtered off and dried, m.p. 160° (transformation at about 122° and darkening at 150°). (Found: C, 13·97; H, 1·47; Hg, 60·69. Calc. for $2{\cdot}(C_6H_7NO){\cdot}3(HgCl_2)$: C, 13·95; H, 1·36; Hg, 58·27%).

The mercury-chloride soln was added drop-wise to the mother-liquor filtered from the previous operation until a white ppt appeared. The solid was quickly filtered off and the acetone soln of mercury chloride was added to the clear liquid and gave a pure white crystalline solid, m.p. 109–110°. (Found: C, 19·12; H, 1·75; Hg, 52·58. Calc. for $C_6H_7NO{\cdot}HgCl_2$: C, 18·93; H, 1·85; Hg, 52·70%). The fractional precipitation was unsuccessful when water was used as solvent.

(c) *With* 1,6-*dimethyl*-3-*pyridone*. This was obtained by mixing acetone solns of the two components. The ppt was crystallized from MeOH-ether as white needles, m.p. 126°. (Found: C, 21·67; H, 2·42; Hg, 50·54. Calc. for $C_7H_9NO{\cdot}HgCl_2$: C, 21·20; H, 2·30; Hg, 50·83%).

(d) *With* 1-*methyl*-4-*pyridone*. The fractional precipitation as described in (b) was used. The first product was crystallized from acetone-ether as white crystals, m.p. 117–118° (micro-crystals in the melt). (Found: C, 29·69; H, 2·68; Hg, 40·75. Calc. for $2(C_6H_7NO){\cdot}HgCl_2$: C, 29·43; H, 2·88; Hg, 40·97%). The second product was also crystallized from acetone-ether, white crystals, m.p. 129° (micro-crystals in the melt). (Found: C, 18·14; H, 1·94; Hg, 51·20. Calc. for $C_6H_7NO{\cdot}HgCl_2$: C, 18·93; H, 1·85; Hg, 52·70%). This product is likely to correspond to that described by Tschitschibabin.[7] When water is used as solvent the product does not show a constant stoichiometry; this material might be a mixture of the two compounds described above.

### *Hydroquinone complexes*

(e) *With* 1-*methyl*-2-*pyridone*. The ppt from an acetone soln was crystallized from acetone-ether, m.p. 115–116°, ((lit.[8] 116–117°).

(f) *With* 1-*methyl*-3-*pyridone*. Equimolar concentrated solns in acetone were mixed in 1:1 ratio and diluted with excess ether. The mixture was cooled for 2 hr at −20° and crystallized from acetone-ether, m.p. 129° (Found: C, 65·80; H, 5·93; N, 6·33. Calc. for $C_{12}H_{13}NO_3$: C, 65·74; H, 5·98; N, 6·39%).

(g) *With* 1-*methyl*-4-*pyridone*. The same procedure as in (f) was followed, m.p. 164–165°. (Found: C, 65·61; H, 6·01; N, 6·39. Calc. for $C_{12}H_{13}NO_3$: as above).

(h) 1,6-*Dimethyl*-3-*pyridone*. The same procedure as in (f) was followed. White crystals were obtained from MeOH, m.p. 168°. (Found: C, 64·66; H, 6·04; N, 4·30. Calc. for $C_{19}H_{21}NO_5$: C, 64·66; H, 6·16; N, 4·08%).

Methanolic concentrated solns of the two compounds were mixed and the ppt crystallized from MeOH, m.p. 195–6°. (Found: C, 66·83; H, 6·81; N, 8·11. Calc. for $C_{20}H_{24}N_2O_4$: C, 67·39; H, 6·79; N, 7·86%). The same

Table 3. Experimental quantities[a] used for calculating the dipole moment[b] of N-methyl-3-pyridone[c] in dioxan[d] solution

| $\alpha$ | $\beta$ | $\gamma$ | $\mu$, (D) | mean value of $\mu$, (D) |
|---|---|---|---|---|
| $58{\cdot}00 \pm 4{\cdot}00^e$ | $-0{\cdot}45 \pm 0{\cdot}27^f$ | $0{\cdot}59 \pm 0{\cdot}43^g$ | $7{\cdot}11 \pm 0{\cdot}29$ | $7{\cdot}17 \pm 0{\cdot}49$ |
| $60{\cdot}00 \pm 6{\cdot}00$ | $-0{\cdot}32 \pm 0{\cdot}28$ | $0{\cdot}59 \pm 0{\cdot}43$ | $7{\cdot}23 \pm 0{\cdot}40$ | |

[a] The quantities $\alpha$, $\beta$ and $\gamma$ are usually defined as follows: $\alpha = d\epsilon_{12}/d\omega_2$ with $\epsilon_{12}$ the dielectric constants and $\omega_2$ the solute weight fraction; $\beta = dv_{12}/d\omega_2$ with $v_{12}$ the specific volumes and $\gamma = dn_{12}/d\omega_2$ with $n_{12}$ the refractive indices.

[b] The dipole moment has been determined according to the method of Halverstad and Kumler as described by Bradford Thompson.*

[c] N-methyl-3-pyridone has been prepared as previously described.[1,4]

[d] Dioxan was purified by alumina column chromatography and then distilled over sodium.

[e] The dielectric constants were measured with a dipolemeter WTW type DM 01 using a DFL1 cell.

[f] The specific volumes were obtained with a digital densimeter Anton Paar K. G. type DMA 02.

[g] The refractive indices were measured with a Precision Refractometer Bausch and Lomb type 33-45-02, sodium lamp.

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*H. Bradford Thompson, *J. Chem. Educ.* **43**, 66 (1966).

deuterated product was obtained by repeated crystallization from MeOD and by combination of the basis with $d_2$-Hydroquinone.

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## REFERENCES

[1] L. Paoloni, M. L. Tosato and M. Cignitti, *Theor. Chim. Acta Berl.* **14**, 221 (1970)

[2] G. Berthier, B. Lévy and L. Paoloni, *Ibid.* **16**, 316 (1970)

[3] H. G. Benson and J. N. Murrell, *J. Chem. Soc. Faraday Trans. II* **68**, 129 (1972)

[4] M. Cignitti and L. Paoloni, *Theor. Chim. Acta Berl.* **25**, 277 (1972)

[5] L. Paoloni and G. B. Marini-Bettolo, *Gazz. Chim. Ital.* **89**, 1972 (1959)

[6] D. Cook, *Canad. J. Chem.* **41**, 515 (1963); **43**, 741, 749 (1965)

[7] A. A. Tschitschibabin and E. D. Ossetrowa, *Ber. Dtsch. Chem. Ges* **58**, 1708 (1925)

[8] B. S. Thyagarajan, K. Rajagopalan and P. V. Gopalakrishnan, *Chem. & Ind.* 1887 (1966)

[9] B. S. Thyagarajan, K. Rajagopolan and P. V. Gopalakrishnan, *J. Chem. Soc.* (B) 300 (1968)

[10] K. Mecklenborg and M. Orchin, *J. Org. Chem.* **23**, 1591 (1958)

[11] R. A. Coburn and G. O. Dudek, *J. Phys. Chem.* **72**, 1177, 3681 (1968)

[12] D. Hadzi and A. Novak, *Infrared Spectra of, and Hydrogen Bonding in, Some Acid Salts of Carboxylic Acids*. University of Ljubljana (1960)

[13] R. Blinc, D. Hadzi and A. Novak, *Z. Electrochem.* **64**, 567 (1960)

[14] J. A. Ibers and W. C. Hamilton, *Hydrogen Bonding in Solids* p. 85–88. Benjamin, New York (1968)

[15] A. Hidalgo and C. Otero, *Spectrochim. Acta* **16**, 528 (1960)

[16] D. Hadzi, *Pure and Appl. Chem.* **11**, 435 (1965)

[17] L. Paoloni, *Gazz. Chim. Ital.* **87**, 408 (1957)

[18] G. A. Ward, *International Laboratory* 72 (1971)

[19] H. von Pechmann and O. Baltzer, *Ber. Dtsch. Chem. Ges* **24**, 3149 (1891)

[20] G. La Manna and M. Cignitti, *Gazz. Chim. Ital.* **102**, 325 (1972)