Tetrahedron Letters No.33, pp. 3695-3698, 1968. Pergamon Press. Printed in Great Britain.

MOLECULAR COMPLEXES OF ACETYLENE ALCOHOLS WITH n- AND π-DONORS

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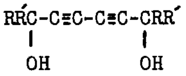
(Received in Japan 29 February 1968; received in UK for publication 24 May 1968)

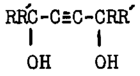
In the course of study on acetylene alcohols we have found that 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (Ia) and 1,1,4,4-tetraphenylbut-2-yne-1,4-diol (IIa) formed crystalline complexes with various n-* and π-donors by definite ratio. The most interesting complexes were derived from Ia and haloalkanes such as carbon tetrachloride, chloroform and methylene chloride. Infrared spectra showed that the complexes have strong hydrogen-bonding.

Among eight kinds of acetylene alcohols tested, tetraphenyl di and monoacetylene diols Ia, IIa formed the complexes but not other ones.



$$\underset{OH}{RR'C}-C\equiv C-C\equiv C-\underset{OH}{CRR'}$$

I a, b, c, d, e, f



$$\underset{OH}{RR'C}-C\equiv C-\underset{OH}{CRR'}$$

II a, f

a: $R=R'=C_6H_5$; b: RR'=9-fluorenyl; c: $R=C_6H_5$, $R'=p\text{-}NO_2\text{-}C_6H_4$;

d: $R=C_6H_5$, $R'=CH_3$; e: $R=C_6H_5$, $R'=H$; f: $R=R'=CH_3$

Recrystallization of Ia or IIa from n- or π-donors afforded the complexes containing the corresponding donor. Both Ia and IIa formed the complexes with most n-donors employed: ketone, aldehyde, ester, ether, amide, amine, nitrile, sulphoxide and sulphide. However, Ia was different from IIa in the following fashions. Although Ia formed the complexes with many

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* As far as we are aware, two complexes of monoacetylene diol with dicyclohexylamine(1) and with dioxane(2) have been isolated without further structural study.

n-donors bearing various types of substituents around donor center in the ratio[*] of 1:2 and the complexes showed clear mp, IIa did only with structurally symmetrical ones in 1:1 ratio and did not show clear mp. For example, Ia formed the 1:2 complexes with all ketones which are shown in the TABLE 1. On the other hand, IIa formed the complexes only with acetone, cyclopentanone and cyclohexanone in 1:1 ratio.

With stronger donors, amine, amide and sulphoxide such those listed in the TABLE 2, both Ia and IIa formed the complexes.

TABLE 1. Melting Point of the 1:2 Complex of Ia and Ketone

ketone	mp (°C)	ketone	mp (°C)	ketone	mp (°C)
acetone	107	p-ethylacetophenone	63	cyclohexanone	95-97
diethyl ketone	73-75	dibenzyl ketone	84-85	2-methylcyclohexanone	82-83
acetophenone	94-95	cyclopentanone	94-95		

TABLE 2. Melting Point of the 1:2 Complex of Ia and Amine, Amide, Sulphoxide

amine	mp (°C)	amine	mp (°C)	amide, sulphoxide	mp (°C)
diethylamine	99-101	aziridine	92	formamide	100-102
triethylamine	59-60	β-phenylethylamine	68-69	N,N-dimethylformamide	107
piperidine	118-119	pyridine	99	dimethyl sulphoxide	175-178
pyrrolidine	128-130	aniline	89-90		

As π-donor, olefine, acetylene and aromatic hydrocarbon were employed. With cyclohexene, 1-methylcyclohexene, phenylacetylene, benzene, toluene, ethylbenzene, o- and p-xylene, styrene, Ia formed 1:1 complexes, showing no clear mp. However, IIa did not form complex with any of those.

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[*] Molar ratio of donor to acetylene alcohol in the complexes was determined by analysis, nmr and by weight loss after heating the complexes at 80° (1 mm).

The most interesting complexes were derived from Ia and haloalkanes such as carbon tetrachloride, chloroform, methylene chloride, ethyl bromide and methyl iodide. With those the complexes of Ia, but not of IIa, were obtained in 1:2 ratio, showing no clear mp.

Since the molar ratio of donor to acetylene alcohol depends on the type but not on the size of the donor molecule, and alkanes do not form complex, those complexes are probably not clathrate compounds but complexes of charge-transfer type. Infrared studies gave further proof for the structure.

In cyclohexane which was inert for complex formation, νOH of both Ia and IIa appeared at 3610 cm^{-1}, however, those of all complexes shifted toward lower frequency. The value of the shift recorded in KBr disk for the complexes of Ia with the following donors were shown: acetone(195 cm^{-1}), cyclopentanone(292), cyclohexanone(312), tetrahydrofuran(330), acetonitrile (204), N,N-dimethylformamide(282), dimethyl sulphoxide(510) and pyridine(580 and 850). The comparable value was observed for a solution of Ia, for example, in tetahydrofuran(304 cm^{-1}) and in acetonitrile(185). Although those bands were assigned to hydrogenbonded νOH with using the complexes derived from Ia-d_2 or IIa-d_2 instead of Ia or IIa, contribution of Fermi resonance would not be excluded in some complexes. Even in those complexes, the presence of hydrogen-bonding was proved furthermore by the following observation. With adding of acetone to a solution of Ia-2 acetone complex 6.3 x 10^{-3} moles in 1 l. chloroform, so as to become to contain 50 and 100 times of acetone, ε of νOH at 3586 cm^{-1} decreased from 202 to 167 and finally to 137.

The most interesting complexes 2Ia-haloalkane showed also the shift of νOH. For solutions of Ia in carbon tetrachloride, chloroform, methylene chloride, ethyl bromide and in methyl iodide, νOH appeared at 3584, 3586, 3575, 3523 and 3519 cm^{-1}, respectively. The comparable values of νOH were observed for the complexes in solid state.

Little is known about electron-donor behavior of chloroform, even though its hydrogen-donor ability has been well known. This is the first example of the isolation of the intermolecular complex of carbon tetrachloride based on hydrogen-bonding. From those results it is shown that even carbon tetrachloride is not inert against electron-acceptor as has been suggested.(3)

Acknowledgment. We wish to thank Professor M. Nakagawa for his interest. We also thank Professor M. Ōki for helpful discussions and mesurements of some of the infrared spectra.

References

1. M. Nakagawa and T. Akagami, Bull. Chem. Soc. Japan 33, 433 (1960).
2. W. Ried, W. Schlegelmilch and S. Piesch, Chem. Ber. 96, 1221 (1963).
3. U. Liddel, Ann. N. Y. Acad. Sci. 69, 70 (1957).