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# Vibrational assignment of *para*-dimethylaminobenzil and its <sup>18</sup>O-substituted derivative

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#### Abstract

The results of FTIR and Raman spectroscopic investigations into *para*-dimethylaminobenzil and its <sup>18</sup>O-substituted derivative are presented and a preliminary assignment proposed on the basis of ab initio quantum chemical calculations. © 1997 Elsevier Science B.V.

Keywords: para-Dimethylaminobenzil; Ab initio; FTIR spectroscopy; Raman spectroscopy

#### 1. Introduction

This work is a part of a current investigation of the vibrational dynamics of aromatic  $\alpha$ -diketones and some of their isotopic isomers and *meta*- and *para*-phenyl substituted derivatives. Interest in the investigation of this group of molecules also arises from the fact that some  $\alpha$ -diketones have good non-linear optical properties [1]. A wealth of experimental infrared and Raman vibrational data is available for the unsubstituted benzil, the so-called "organic quartz" [2]. On the other hand, benzil and substituted benzils convert lightly into the corresponding anion radicals and dianions by electrochemical reduction and by reduction with alkali metals in vacuo [3].

In our previous paper [4] a complete vibrational assignment of benzil and its <sup>18</sup>O-substituted derivative was performed. So far no assignment of the

vibrational bands of *para*-dimethylaminobenzil and its <sup>18</sup>O derivative has been reported.

In this paper we present the results of FTIR and Raman spectroscopic investigations and propose a preliminary assignment on the basis of ab initio quantum chemical calculations which are in progress.

# 2. Experimental

The starting compound was synthesized by mixed benzoin condensation of benzaldehyde and 4-dimethylaminobenzaldehyde followed by oxidation with SeO<sub>2</sub>. The preparation of the <sup>18</sup>O compound was carried out according to Roberts and Urey [5]. The isotopic content, determined by mass spectrometry, was 70.04 at% <sup>18</sup>O.

Vibrational spectra of the title compound were measured in the solid state in the Raman (4000– $100 \text{ cm}^{-1}$ ) and infrared (4000– $100 \text{ cm}^{-1}$ ) regions.

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Table 1		
Vibrational assignment of para-dimethy	ylaminobenzil and its	<sup>18</sup> O-substituted derivative

$v_i/\mathrm{cm}^{-1}$	para-Dimeth	ylaminobenzil	para-Dimethy	para-Dimethylaminobenzil- <sup>18</sup> O	
	IR	Raman	IR	Raman	
1	3098	3097	3096	3098	20a
2	-	3085	_	3085	20a
3	_	3074	_	3074	20b
4	3066	-	3066	-	2
5	-	3061	_	3061	2
6	3051	3054	3052	3054	7a
7	3033	3036	3033	3036	7a
8	-	3024	_	3024	13
9		2996	_	2996	13
10	2921	2921	2922	2921	$\nu(CH_2)$
11	2840		2840		$\nu(CH_2)$
12	2861	_	2861	_	$\nu(CH_3)$
13	2823	-	2823	_	v(CH <sub>3</sub> )
14	2823	_	2823	_	$\nu(CH_{a})$
15	2812	_	2817	_	$\nu(\mathbf{CH}_{-})$
15	1671	-	1647	-	$\nu(C \Pi_3)$
10	1635	16/1	1042	1041	$\nu (C=0)$
17	1603	1602	1011	1606	₽ (C=O)
10	1602	1602	1590	1590	6a 9-
19	1594	1590	1594	1590	82
20	1579	1584	1579	1584	80
21	-	1552	-	1543	86
22	1493	-	1492	-	19a
23	-	1484	-	1484	19a
24	-	1450	-	1451	196
25	1439	1442	1438	1442	19b
26	1414	1415	1414	1415	Comb.
27	1381	1379	1379	1380	δ(CH <sub>3</sub> )
28	1343	1340	1343	1340	14
29	1330	1332	1332	1329	14
30	-	1319	-	1319	3
31	1300	1301	1301	1300	3
32	1234	1232	1234	1232	<b>e</b> <sub>2</sub>
33	1190	1190	1189	1189	9a
34	1170	1172	1170	1172	<b>e</b> <sub>1</sub>
35	_	1161	-	1161	9Ь
36	1135	1136	1135	1135	18a
37	1070	1071	1070	1071	18a
38	1050	1049	1050	1049	$\nu(CO-CO)$
39	1026	1024	1026	1024	18b
40	1001	1001	1001	1001	1(breathing)
41	995	996	995	996	5
42	_	978	_	978	17a
43	_	945	_	946	18b
44	_	931	_	931	100 17h
45	880	951	880	887	170 d.
	00U 827	825	826	002 82 <b>5</b>	u <sub>2</sub> 10a
40	705	706	705	704	10a
+/ 18	נעז 171	790 777	ני <i>נ</i> ו 1 רק	771	11
-+0 /0	7/1	7/2	7/1	7/1	d II
47 50	710	715	/+10 710	740	u <sub>1</sub>
50 51	/18	/15	/18	/15	4
51	703	-	705	-	4

Table 1 Continued

<i>v<sub>i</sub></i> /cm <sup>-1</sup>	para-Dimethylaminobenzil		para-Dimethylaminobenzil- <sup>18</sup> O		Assignment
	IR	Raman	IR	Raman	
52		684	_	684	6a
53	673	671	673	671	6a
54	632	633	632	633	6b
55	615	616	616	615	6b
56	600	600	593	593	δ(C=O)
57	-	492	-	492	X-sens.
58	-	479	_	479	16a
59	-	455	-	455	16a
60	446	447	447	446	16b
61		437	-	437	16b
62	365	366	365	366	X-sens.
63	-	330	-	323	γ(C=O)
64	266	262	266	262	$\delta(O=C-CO)$
65	209	211	209	211	15(X-sens.)
66	208	208	209	209	δ(Ph…pl…Ph)
67	-	205	-	205	δ(Ph…pl…Ph)
68	141	141	141	141	$\gamma(Ph\cdots pl\cdots Ph)$
69		136	-	136	$\gamma(Ph\cdots pl\cdots Ph)$
70	123	123	123	123	$\gamma(Ph\cdots pl\cdots Ph)$
71	118	118	118	118	$\tau$ (Ph-COCOPh)
72	102	102	102	102	$\tau$ (PhCO-COPh)
73	-	92	-	92	$\tau(-C_6H_4-N(Me)_2)$
74	-	76	-	76	$\tau(N-Me)$
75		71	-	71	$\tau(\text{CO-Ph})$
76		60	-	59	Latt. vibr.
77		57	-	57	Latt. vibr.
78		46	-	47	Latt. vibr.

The differential infrared dichroic spectra (4000–400 cm<sup>-1</sup>) of oriented polycrystalline layers were also recorded and studied. The infrared spectra of chloroform solutions were measured in the range 4000–400 cm<sup>-1</sup>.

The mid-infrared spectra of powders in KBr pellets were recorded with a Bruker IFS 113v FTIR spectrometer equipped with a high-intensity Globar source, Ge/KBr beamsplitter and DTGS detector in the 4000– 400 cm<sup>-1</sup> region. The far-infrared spectra were recorded in polyethylene pellets on the same instrument equipped with a high-pressure Hg arc lamp, a Mylar beamsplitter and DTGS detector in the 600– 100 cm<sup>-1</sup> region. All spectra were recorded at room temperature at a resolution of 1 cm<sup>-1</sup> and 100 scans. Raman spectra of a polycrystalline powder were measured on a Bruker IFS 66 FTR spectrometer using a 1064 nm Neodym YAG laser with power 159 mW at room temperature in the 4000–50 cm<sup>-1</sup> frequency range. The spectra were measured at a resolution of 2 cm<sup>-1</sup> and 100 scans.

### 3. Results and discussion

The observed bands and their assignment are given in Table 1. The assignment of the molecules studied (Fig. 1) was done on the assumption of  $C_1$  molecular symmetry.

The assignment of the vibrational bands was performed using the group vibrational concept, isotopic shifts and polarization features of the normal modes.

The new spectral information concerns the infrared and Raman spectra of both compounds.

In the 3100-2900 cm<sup>-1</sup> region nine frequencies were expected: five frequencies belonging to the  $\nu$ (C-H) phenyl ring vibrations and four belonging to



Fig. 1. Molecular structure of para-dimethylaminobenzil determined by ab initio calculations at the RHF/STO-3G level.

the *para*-substituted benzene ring. In the 2900–2800 cm<sup>-1</sup> frequency region six frequencies were expected, all belonging to stretching vibrations of the two methyl groups. All 15 frequencies were assigned to the corresponding  $\nu$ (C–H) vibrational modes.

The asymmetric C=O stretching vibration in the infrared spectra, as seen with relatively strong intensity in all substituted benzils, appears at 1671  $\text{cm}^{-1}$ and in the Raman at 1672 cm<sup>-1</sup>. The symmetric stretching vibration of the para-dimethylaminobenzil was found at 1635  $\text{cm}^{-1}$  (IR) and 1641  $\text{cm}^{-1}$  (Raman). The <sup>18</sup>O substitution prominently influences only the characteristic carbonyl frequencies. The  $v^{as}(C=O)$ appears at 1642  $\text{cm}^{-1}$  in the IR and 1641  $\text{cm}^{-1}$  in the Raman. The symmetric stretching vibration was found at 1616  $\text{cm}^{-1}$  in the IR and 1611  $\text{cm}^{-1}$  in the Raman spectrum. The in-plane deformation vibration,  $\delta$ (C=O), was found at 600 cm<sup>-1</sup> while the out-of-plane  $\gamma$ (C=O) lies at 323 cm<sup>-1</sup>. The <sup>18</sup>O isotopic shifts, 7 cm<sup>-1</sup> each for  $\delta$ (C=O) and  $\gamma$ (C=O) and 30 cm<sup>-1</sup> for  $\nu^{as}(C=O)$  and 20 cm<sup>-1</sup> confirm the band assignment.

All vibrational motions connected with both carbonyl groups were assigned unambiguously. The vibrational assignment of *para*-dimethylaminobenzil is like that of unsubstituted benzil [4], but some differences remain, especially for C=O in-plane and out-of-plane vibrations.

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