

Infrared Linear Dichroism on 1,5-Diphenyl-1,3,5-pentanetrione Aligned in Stretched Polyethylene

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The title compound, aligned in uniaxially stretched polyethylene (PE) sheets has been investigated by infrared linear dichroism (LD) spectroscopy. It has been possible to observe 38 vibrational transitions and to determine orientation factors for several of the transition moment directions. The only reasonable interpretation of the experimental data is that the observed molecule has C_{2v} -symmetry and that the compound adopts the symmetrical dienol form when dissolved in PE. The IR LD spectra do not indicate the presence of keto or enol forms, in contrast with the results of previous IR investigations using Nujol mull as the solvent.

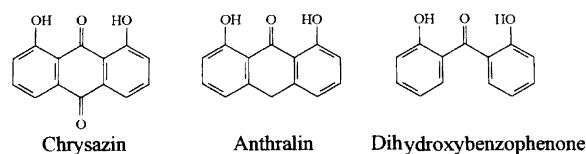
1,5-Diphenyl-1,3,5-pentanetrione or dibenzoylacetone (DBAc) has been a compound of interest for several years. One reason is that DBAc is a member of an important class of ligands, the *cis*- β -triketones, which forms complexes with metal ions.¹⁻⁴ Another reason is the interesting structural dynamics observed for this compound which has the ability to undergo keto-enol-tautomerism, existing in solution as an equilibrium mixture of triketo-, enol- and dienol-forms. These equilibria and the determination of the dominant form in the various media have been the subject of several papers.^{2,5-10}

The equilibrium for DBAc can be formulated as shown in Scheme 1. The triketo form (I), the non-planar enol form, (II) and the symmetrical dienol form (III).

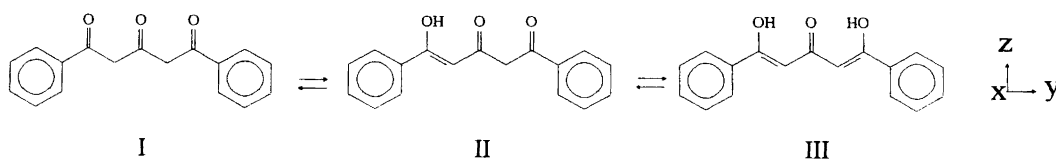
It is possible to formulate a number of tautomers; however, it has been indicated that enolisation of the terminal carbonyl groups is favoured.⁹ NMR studies have demonstrated that the dienol form (III) is the dominant tautomer in solvents like (²H)chloroform, (²H₂)dichloromethane and (²H₆)benzene. In (²H₆)benzene the triketo-form (I) is no longer detected.^{2,6,7,9-11} X-Ray diffraction and ¹³C NMR studies, using the 'magic angle spinning' technique, indicate

that DBAc in the solid state exists primarily on the dienol form (III).^{12,13}

In the symmetrical dienol form the compound has the same intramolecular hydrogen bonding system as observed in 1,8-dihydroxy-9,10-anthraquinone (chrysazin), 1,8-dihydroxy-10*H*-anthracenone (anthralin) and 2,2'-dihydroxybenzophenone. Chrysazin has attracted much attention because the compound is a chromophore in anthracyclines^{14,15} and anthralin is a potent antipsoriatic drug.^{16,17}



This paper presents an IR linear dichroism spectroscopic investigation of DBAc aligned in stretched polyethylene (PE) sheets. By this technique one may analyse the orientation factors for the transition moment directions and from this obtain information on molecular alignment. This type of information makes it possible to draw conclusions with regard to the possible presence of



Scheme 1.

molecular symmetry elements and to molecular geometry of DBAc.

Experimental

DBAc ($C_{17}H_{14}O_3$) [Chem. Abstr. No. 1467-40-9] was synthesised according to descriptions¹⁸ and was crystallised from ethanol. The yield of yellow crystals was 65%, with a melting point of 109–110 °C (106–110 °C¹⁹). Two independently synthesised samples were used. The purity was checked by ¹H NMR spectroscopy [250 MHz, CDCl₃, TMS(1%), Merck UVASOL]: δ 4.10 (s, 2 H, methylene H–enol form), 4.32 (s, 4 H, methylene H–keto form), 6.01 (s, 2 H, methine H, dienol form), 6.30 (s, 1 H, methine H, enol form), 7.42–8.04 (m, 30 H, aromatic H– keto, enol, dienol form), 14.76 (s, 2 H, chelate H, dienol form), 15.83 (s, 1 H, chelate H, enol form). The spectrum clearly illustrates the existence of all three tautomers in chloroform. The assignment is in agreement with literature data.^{2,6,9,10}

The LD spectra were measured for samples in stretched low-density polyethylene (PE) sheets. The sheets used were 1.5 mm thick polyethylene obtained by melting together several layers of thin sheets. To remove additives and to ensure purity the sheets were washed in chloroform (Merck UVASOL) before use. DBAc was introduced into the PE by placing the sheet in a concentrated solution of DBAc in chloroform. The sheet was left in the solution for a few days at room temperature. After removal of the sheet from the solution the chloroform was evaporated off and the sample stretched uniaxially around 400%. Methanol (Merck UVASOL) was used to remove crystals from the sheet surface. A reference sheet without treatment with DBAc was treated in exactly the same way. A second procedure was also used in which the PE sheets were stretched before introduction of DBAc. This procedure resulted in a poor alignment of the molecules but more reproducible results.

Spectra of DBAc in KBr and Nujol mull were also recorded. The spectra are not shown but the KBr data are listed in Table 1. The IR spectra were recorded on Perkin–Elmer 1700 and 2000 FTIR instruments equipped with aluminium grid polarisers.

All LD spectra were recorded at room temperature in the spectral region 400–4000 cm^{-1} with a resolution of 2 cm^{-1} . The spectra presented in Fig. 1 were the average of 40 scans. In the LD investigation two experiments were performed, one with the light polarised parallel and one perpendicular to the uniaxial stretching direction of the sheet. Sample and reference spectra were recorded independently, using identical procedures. Light polarised parallel to the stretching direction of the sheet resulted in the E_U spectrum, and light polarised perpendicular to the stretching direction resulted in the E_V spectrum. In all cases the beam was perpendicular to the surface of the sheet. Subtraction of the reference spectra was performed manually. The resulting LD spectra are shown in Fig. 1. The regions with strong PE absorption

(700–750, 1340–1380 and 1420–1485 cm^{-1}) were left blank. The LD spectra are presented only in the spectral region 400–2000 cm^{-1} , since only limited information was available in the region 2000–4000 cm^{-1} . The two small blank areas around 670 and 1215 cm^{-1} are due to traces of chloroform remaining in the sheets.

IR linear dichroism (LD) spectroscopy

As indicated above two absorption curves $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ can be obtained from the uniaxially stretched PE sample, one with the electric vector of the light parallel and one perpendicular to the uniaxial stretching direction of the PE sheet shown in Fig. 1. For uniaxial samples the dichroic ratio $d_i = E_U(\tilde{\nu}_i)/E_V(\tilde{\nu}_i)$ for each non-overlapping transition i is related to the orientation factor K_i through the equation $K_i = d_i/(2 + d_i)$. The orientation factor is defined by $K_i = \langle \cos^2(M_i, U) \rangle$, the angle brackets indicating averaging over all molecules in the beam of the light while (M_i, U) is the angle between the transition moment of transition i and the uniaxial stretching direction of the sample.²⁰ K_i is the available experimental information concerning the transition moment directions relative to the uniaxial stretching direction. Transition moment directions are dictated by the molecular symmetry; e.g., a molecule with C_{2v} symmetry has allowed transitions polarised along the three mutually perpendicular symmetry axes x , y and z . If DBAc(III) were approximately planar the molecular symmetry should effectively correspond to C_{2v} . The observed orientation factors should thus adopt only three values corresponding to the three possible transition moment directions. $K_s = \langle \cos^2(s, U) \rangle$, $s = x, y, z$. From their definition it follows that $\Sigma K_s = K_x + K_y + K_z = 1$.

A molecular geometry without two mutually perpendicular axes or planes of symmetry allows an infinite number of possible transition moment directions. The transition moments lie in a variety of different directions and the orientation factors will not fall into three distinct groups. This is the situation expected for, e.g., the DBAc(II) geometry. Molecules embedded in stretched PE tend to align according to the molecular shape; for DBAc(III) the ‘long’ in-plane axis (y) tends to align better with the stretching direction than the ‘short’ in-plane axis (z) while the out-of-plane axis (x) has the poorest alignment. It follows that $K_y \geq K_z \geq K_x$.²⁰

If transitions overlap, the K values can frequently be obtained by the TEM procedure.²⁰ According to this, linear combinations of the two experimental curves $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ can be constructed until the contribution from the transition in question disappears. Here we use the following eqns. (1) and (2).²⁰

$$E_{-y}(\tilde{\nu}) = E_V(\tilde{\nu}) - (1/d)E_U(\tilde{\nu}), \quad \text{where } d = d_y \quad (1)$$

$$E_{-z}(\tilde{\nu}) = E_U(\tilde{\nu}) - dE_V(\tilde{\nu}), \quad \text{where } d = d_z \quad (2)$$

In the curve $E_{-y}(\tilde{\nu})$ contributions from transitions polarised along the y axis are absent but transitions polarised along the z and x axes are seen as positive

Table 1. IR LD and IR absorption data for 1,5-diphenyl-1,3,5-pentanetrione (III) at room temperature. The LD data are for samples in stretched PE and the IR data in KBr.

No.	$\tilde{\nu}_{PE}^a$	I^b	K^c	K'^d	Pol. ^e	Sym. ^f	$\tilde{\nu}_{KBr}^g$
							410
							428
							447
1	470	≈ 1	—	—	y	b ₂	471
							494
2	578	11	0.71	0.61	y	b ₂	578
3	617	1	0.71	0.57	y	b ₂	616
4	650	4	0.18	0.21	z	a ₁	651
5	657	4	0.09	0.14	x	b ₁	655
6	686	20	0.09	0.13	x	b ₁	684
	PE						691
	PE						718
	PE						723
	PE						754
7	774	33	0.08	0.12	x	b ₁	775
8	788	≈ 1	(0.21)	(0.25)	z	a ₁	790
9	815	10	0.10	0.14	x	b ₁	818
10	841	≈ 1	(0.22)	—	z	a ₁	839
11	864	7	0.71	—	y	b ₂	861
							878
12	891	9	0.10	0.13	x	b ₁	897
13	921	3	0.10	0.11	x	b ₁	925
							973
14	986	7	0.18	0.25	z	a ₁	983
15	1000	3	0.71	—	y	b ₂	999
16	1002	≈ 1	0.18	—	z	a ₁	
17	1027	≈ 1	—	—	y	b ₂	1030
18	1066	6	—	—	y	b ₂	1063
19	1072	7	—	—	y	b ₂	1073
20	1083	6	—	—	z	a ₁	1080
21	1097	6	—	—	y	b ₂	1100
22	1154	40	0.71	0.62	y	b ₂	1157
23	1162	30	0.71	0.63	y	b ₂	1163
24	1184	13	0.68	0.59	y	b ₂	1182
							1192
25	1234	1	0.18	—	z	a ₁	1238
26	1250	4	0.18	0.25	z	a ₁	1253
27	1276	16	—	0.60	y	b ₂	1282
28	1292	5	—	0.43	y	b ₂	
29	1295	3	—	—	z	a ₁	1293
30	1308	5	—	0.39	y	b ₂	1300
31	1331	—	—	—	y	b ₂	1330
	PE						1341
	PE						1379
32	1403	≈ 3	—	0.57	y	b ₂	1409
	PE						1437
	PE						1450
	PE						1468
33	1493	44	0.70	0.55	y	b ₂	1494
34	1558	73	0.70	0.61	y	b ₂	1558
35	1568	67	0.70	0.61	y	b ₂	1568
36	1592	67	0.70	0.61	y	b ₂	1596
37	1604	33	0.70	0.57	y	b ₂	1602
38	1632	9	—	—	z	a ₁	1634
							1683

^aWavenumber in cm^{-1} . Values in italics indicate overlapped peaks. ^bIsotropic absorbance $E_{\text{iso}} = (E_U + 2E_V)/3$, E_U and E_V are the absorbance $\times 10^2$. Values in italics indicate overlapped peaks estimated from the reduced curves. ^cOrientation factors estimated for the spectra shown (Fig. 1). ^dOrientation factors for a sample prepared according to a different procedure (see the Experimental). The spectra are not shown. ^eAssignment of transition moment directions. ^fIrreducible representations in the C_{2v} point group. The x-axis forms a basis for b₁, the y-axis for b₂ and the z-axis for a₁. ^gData for DBAc in KBr.

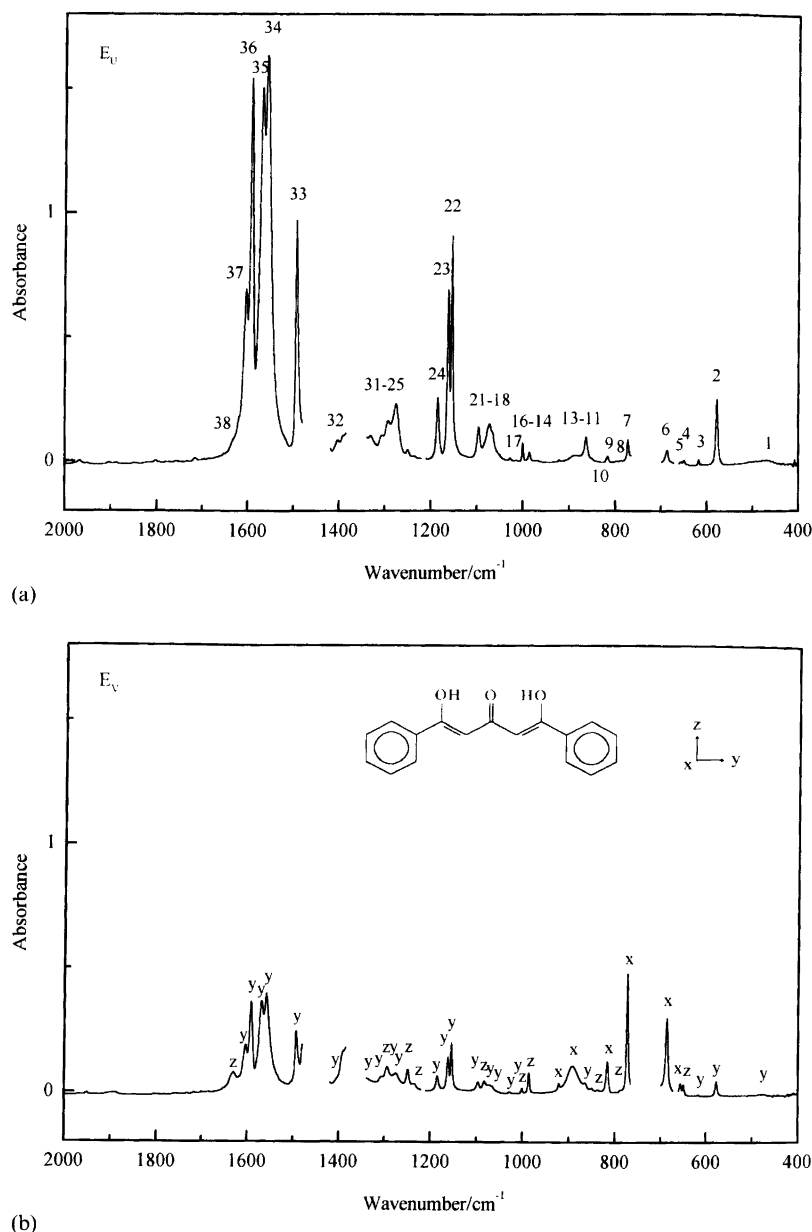


Fig. 1. IR LD absorption curves for DBAc (III) in stretched PE at room temperature. (a) E_U spectrum recorded with light polarised parallel to the stretching direction of the PE sheet, the numbering of the peaks corresponds to the numbers in Table 1; (b) E_V spectrum recorded with the light polarised perpendicular to the stretching direction. The polarisation of the transitions are marked for each peak and can also be found in Table 1.

peaks. In the $E_{-z}(\tilde{\nu})$ curve the contributions from z polarised transitions are absent. Transitions polarised along the y axis are seen as positive peaks while transitions polarised along the x axis are negative. The two curves are shown in Fig.2.

Results and discussion

The two IR LD spectra of DBAc in stretched PE, $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$, are shown in Fig.1. The two LD spectra clearly demonstrate linear dichroism and an efficient molecular alignment consistent with an elongated molec-

ular shape. Thirty-eight observed transitions, their intensity, orientation factors and polarisation are listed in Table 1.

All observed orientation factors fall into three distinct groups with values equal to 0.70(2), 0.19(3) and 0.09(1); the values add up to unity within experimental error. The only reasonable explanation of this observation is that DBAc effectively has a molecular C_{2v} symmetry, corresponding to formula III. The three characteristic K s are therefore assigned $(K_x, K_y, K_z) = (0.09, 0.70, 0.19)$; the labelling of the axes is indicated in Scheme 1. In Table 1 are listed orientation factors obtained from a

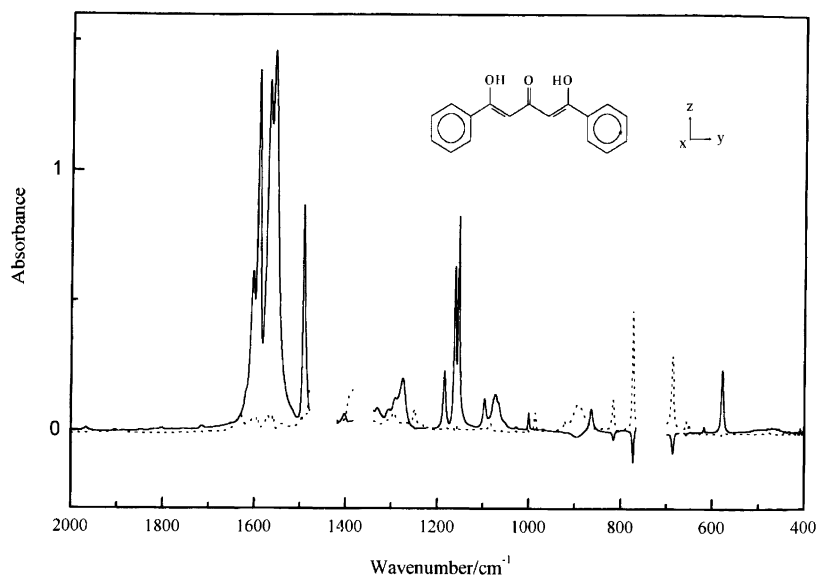


Fig. 2. Reduced absorbance curves. The full curve indicates $E_{-z}(\bar{\nu}) = E_U(\bar{\nu}) - 0.47E_V(\bar{\nu})$ where contributions from z-polarised transitions are absent, while y and x-polarised transitions are seen as positive and negative peaks, respectively. The broken curve is $E_{-y}(\bar{\nu}) = E_V(\bar{\nu}) - 0.21E_U(\bar{\nu})$ where contributions from transitions polarised along the y axis are absent and transitions polarised along z and x axes are seen as positive peaks.

second sample. This sample was prepared in a different way (see the Experimental section) resulting in a poorer alignment of the DBAc molecules in the PE sheet. In this case the K values consist of three groups with values equal to 0.60(3), 0.25(4) and 0.13(2), which add up to unity within experimental error. Once more the orientation factors are consistent with the assumption of C_{2v} symmetry and are assigned as $(K_x, K_y, K_z) = (0.13, 0.60, 0.25)$. In order to analyse overlapping transitions construction of reduced absorption curves may be of great help. Fig. 2 shows two curves, E_{-y} and E_{-z} , each representing spectra in which contributions from y- or z-polarised transitions, respectively, are removed. The reduced curves resolve the more complex structures in the spectra, for example the band cluster in the range 1276–1308 cm^{-1} . This band reveals four transitions, two y-polarised at 1276 and 1292 cm^{-1} , one z-polarised at 1295 cm^{-1} , and one y-polarised transition at 1308 cm^{-1} .

The spectra show no sign of the enol form **II**. In particular, the carbonyl stretching transition expected for the enol form is not observed (see below). The presence of this tautomer would manifest itself as peaks with orientation factors being different from the values mentioned above. Without additional information it is not possible to assign all thirty-eight observed transitions in DBAc(**III**) to particular vibrations or motions. We will therefore focus our attention upon the characteristic vibrations involving the carbonyl and hydroxy groups since the structural discussion is centered on the configuration and conformation of these groups.

The O–H stretching vibrations of the hydroxy groups are not easily observed in the present spectra; these transitions are probably broadened as a result of intramolecular hydrogen-bonding. The carbonyl stretching

vibration, however, is characteristic; it is totally symmetric (a_1) and is therefore polarised along the carbonyl group, in this case along the z-axis. The $\nu(\text{C}=\text{O})$ vibration for conjugated and hydrogen-bonded carbonyl groups is expected between 1580 and 1640 cm^{-1} , according to group frequency tables.

In this spectral region only one z-polarised transition is observed and that is the basis for the assignment of transition No. 38 at 1632 cm^{-1} to the $\nu(\text{C}=\text{O})$ stretching vibration. This assignment is supported by data for related compounds, such as chrysazin, anthralin and 2,2'-dihydroxybenzophenone, all having the same structural arrangement of the hydroxy and carbonyl groups as DBAc(**III**). For these compounds the $\nu(\text{C}=\text{O})$ stretching vibrations are observed at 1627, 1631 and 1626 cm^{-1} , respectively.^{21,22}

There is no sign of transitions in the region 1632–1800 cm^{-1} at higher energy, apparently excluding the existence of a non hydrogen-bonded carbonyl group as expected for the keto (**I**) and enol (**II**) forms. These findings are in contrast with those of Bachlas *et al.*¹ who described a strong, sharp absorption at 1680 cm^{-1} . Their spectrum was recorded in Nujol mull. It has not been possible to reproduce these observations in our laboratory although a weak broad transition at 1680 cm^{-1} is observed in both KBr and Nujol.

The symmetrical and antisymmetrical $\delta(\text{O}-\text{H})$ bending vibrations are of a_1 and b_2 symmetry, respectively, and are expected between 1410 and 1310 cm^{-1} . The weak z-polarised transition, No. 29, at 1295 cm^{-1} is tentatively assigned to the symmetrical O–H bending vibration. One of the transitions, No. 30, 31 or 32 at 1308, 1331 or 1403 cm^{-1} , which are all of b_2 symmetry, might be assigned to the antisymmetrical vibration. Finally the

strong x -polarised transition at 774 cm^{-1} is tentatively assigned to the out-of-plane deformation vibration $\gamma(\text{O-H})$. This is by analogy with assignments of similar peaks for chrysazin at 750 cm^{-1} , 1,4-dihydroxy-9,10-anthraquinone at 780 cm^{-1} and anthralin at 750 cm^{-1} .²¹⁻²³

Conclusions

The orientation factors for the observed transitions consist of three well separated groups and the characteristic values of these groups add up to unity. These findings are in perfect agreement with the assumption that the DBAc molecule has effective C_{2v} symmetry in PE at room temperature. The identification of a $\nu(\text{C=O})$ stretching vibration at 1632 cm^{-1} is in agreement with the presence of a doubly hydrogen-bonded carbonyl group confirming the conclusion that DBAc is in the symmetrical dienol form III. No evidence has been found for the presence of tautomers with a free carbonyl group. This is in contrast with the results from IR and NMR studies in Nujol and benzene.^{1,10} The present results demonstrate that the stretched sheet method is a powerful tool to elucidate molecular structure and symmetry.

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