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The Rotatory Dispersion and Stereochemistry of Organic Compounds. XIV.[1] Nitrobenzylidene Derivatives of Diethyl *d*-Tartrate

Yojiro Tsuzuki, Motoo Koyama and Koko Tanabe

Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

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Anomalous optical rotation has been observed not only with the ortho-nitrobenzylidene derivative of diethyl *d*-tartrate (Tsuzuki, *Bull. Chem. Soc. Japan*, **14**, 35 (1939); *Sci. Pap. I. P. C. Res. (Tokyo)*, **35**, 425, 466 (1939)), but also with some acetylated ortho-nitrophenyl glycosides of the β-type (Capon *et al.*, *J. Chem. Soc.*, **1961**, 5172; Montgomery *et al.*, *J. Am. Chem. Soc.*, **64**, 690 (1942); Snyder *et al.*, *ibid.*, **75**, 1758 (1953); Tsuzuki *et al.*, *Bull. Chem. Soc. Japan*, **40**, 1208 (1967)). To investigate this anomalous effect of the ortho-nitro group the authors have made rotatory dispersion studies on several derivatives of diethyl *d*-tartrate as well as its alkylidene derivatives. Of these compounds examined, the compound (I) with a nitro group in the ortho-position of the phenyl group shows a positive Cotton effect at about 340 mμ, and it has been found that the nitrophenyl group is optically active. Furthermore, in order to inquire into this anomaly the authors have observed the CD, UV and NMR spectra of these compounds, from which it is concluded that the conformations of the acetal rings of all the compounds are nearly equal, and the anomalous dispersion of the compound I at about 340 mμ is assumed to be due to the n→π* transition of the nitro group with a slight shoulder appearing at 325 to 350 mμ. In view of these facts it is considered that the ortho-nitro group is twisted from the plane of the benzene ring caused by the steric hindrance of the bulky acetal ring.

Many years ago one of the authors found in the course of studies on the optical activity of some benzylidene derivatives of diethyl tartrate that the optical rotation was deeply influenced by the position of nitro group,[2,3] namely, the meta- and para-nitrobenzylidene derivatives are normally laevo-rotatory, whereas the corresponding ortho-compound shows a large positive rotation; however, such inversion of rotation can never be observed with the benzylidene derivatives that carry *o,p*-directing hydroxyl group as well as halogen atoms even in the ortho-position.

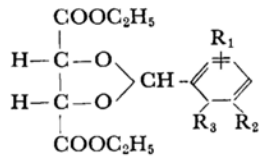
A similar anomalous ortho-nitro effect has also been noticed with other series of compounds. Of late years a number of related papers appeared on the rotation of acetylated nitrophenyl glycosides of the β-type.[4-7] Mislow *et al.*[8] found that 2,2'-dinitrobiphenyls exihibit Cotton effects at 330 mμ, the sign of which is related with the absolute configuration. Nevertheless, the cause of the anomaly has not been elucidated.

With a view to inquiring into this anomalous effect of the ortho-nitro group the authors have made rotatory dispersion studies on several derivatives of diethyl *d*-tartrate as well as its alkylidene derivatives. In order to obtain information on the conformations of these compounds the authors have furthermore observed the circular dichroism (CD), ultraviolet absorption (UV) and nuclear magnetic resonance spectra (NMR). The compounds examined were in total sixteen:

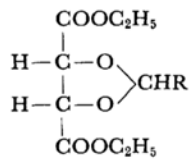
Diethyl *o*-nitrobenzylidene-*d*-tartrate (compound I),
Diethyl *m*-nitrobenzylidene-*d*-tartrate (compound II),
Diethyl *p*-nitrobenzylidene-*d*-tartrate (compound III),
Diethyl 2,5-dimethylbenzylidene-*d*-tartrate (compound IV),

1) Part XIII: Y. Tsuzuki, K. Tanabe, M. Akagi and S. Tejima, This Bulletin, **40**, 628 (1967).
2) Y. Tsuzuki *ibid.*, **14**, 35 (1939).
3) Y. Tsuzuki, *Sci. Pap, I. P. C. Res. (Tokyo)*, **35**, 425 (1939); *ibid.*, **35**, 466 (1939).
4) B. Capon, N. G. Overand and M. Sobell, *J. Chem. Soc.*, **1961**, 5172.
5) E. M. Montgomery, N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **64**, 690 (1942).
6) J. A. Snyder and K. P. Link, *ibid.*, **75**, 1758 (1953).
7) Y. Tsuzuki and K. Tanaka, This Bulletin, **40**, 1208 (1967). Here it was shown by studying the NMR spectra of some anomeric tetra-*O*-acetyl-D-glucopyranosides that the anomalous optical rotatory power should not be attributed to the particular conformation of the aryl group, and in particular the anomaly of *o*-nitrophenyl glucosides seems rather to be attributable to a certain property of the nitro group, such as the field effect of the group exerted upon the anomeric center through space.
8) K. Mislow, M. A. W. Glass, E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962).

Diethyl *m*-methylbenzylidene-*d*-tartrate (compound V),
Diethyl *p*-methylbenzylidene-*d*-tartrate (compound VI),
Diethyl *o*-iodobenzylidene-*d*-tartrate (compound VII),
Diethyl *p*-iodobenzylidene-*d*-tartrate (compound VIII),
Diethyl *o*-chlorobenzylidene-*d*-tartrate (compound IX),
Diethyl *p*-chlorobenzylidene-*d*-tartrate (compound X),
Diethyl methylidene-*d*-tartrate (compound XI),
Diethyl ethylidene-*d*-tartrate (compound XII),
Diethyl vinylidene-*d*-tartrate (compound XIII),
Diethyl benzylidene-*d*-tartrate (compound XIV),
Diethyl α-naphthylidene-*d*-tartrate (compound XV),
and
Diethyl 2-nitro-3,6-dimethylbenzylidene-*d*-tartrate (compound XVI).



I	R_1=*o*-NO_2; R_2, R_3=H
II	R_1=*m*-NO_2; R_2, R_3=H
III	R_1=*p*-NO_2; R_2, R_3=H
IV	R_1=*o*-CH_3; R_2=CH_3; R_3=H
V	R_1=*m*-CH_3; R_2, R_3=H
VI	R_1=*p*-CH_3; R_2, R_3=H
VII	R_1=*o*-I; R_2, R_3=H
VIII	R_1=*p*-I; R_2, R_3=H
IX	R_1=*o*-Cl; R_2, R_3=H
X	R_1=*p*-Cl; R_2, R_3=H
XVI	R_1=*o*-CH_3; R_2=CH_3; R_3=NO_2



XI	R=-H	XIV	R=
XII	R=-CH_3		
XIII	R=-CH_2=CH_2	XV	R=

Fig. 1. Structures of derivatives of diethyl tartrate examined.

Results and Discussion

In Fig. 2 are shown the RD curves of the compounds I, II, III and XIV together with the CD curve of the compound I. The compound I with a nitro group in the ortho position of the phenyl group shows a positive rotation in the region above 350 mμ and, moreover, exhibits a number of Cotton

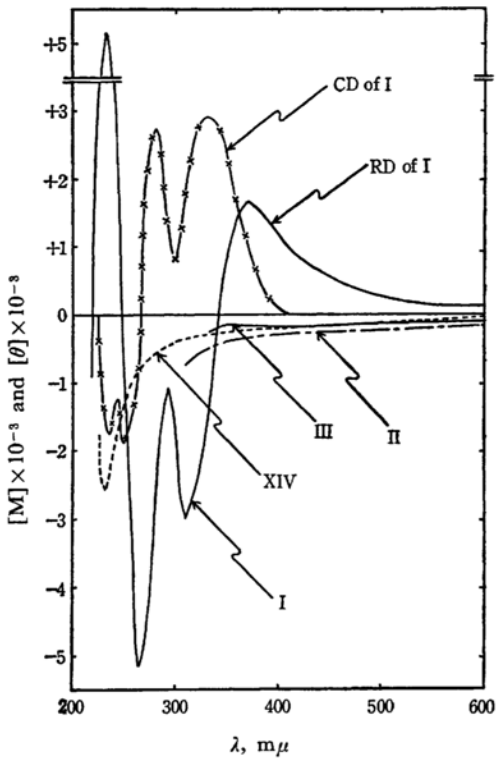


Fig. 2. RD of nitrobenzylidene derivatives and CD of I.

effects, namely two positive effects centered at 340 mμ and 280 mμ and a negative one near 248 mμ. The signs of these Cotton effects are supported by the CD curve I. On the other hand, the meta- and para-nitro derivatives (II and III) both exhibit negative plain RD curves with no anomaly near 340 mμ, which run just along their background curve XIV. The latter two compounds admitted of no RD measurement below 310 mμ due to the strong absorption.

In order to investigate whether the anomalous rotation of the compound I results from the distortion of the acetal ring effected by the steric hindrance due to the ortho-nitro group, the rotatory dispersions of the compounds IV—XVI were measured.

Figure 3 gives the RD curves of the compounds IV, V and VI, which carry a methyl group respectively on the ortho-, meta- and para-positions of the phenyl group. In Fig. 4 are shown the RD curves of the compounds VII, VIII, IX and X with a halogen atom occupying either the ortho- or para-position. Of these compounds no anomaly due to the ortho-substituent was observed. However, the *o*-iodo and *p*-chlorobenzylidene derivatives VII and X exhibit Cotton effects, though very weak, near 280 mμ. The other compounds, as are shown in Figs. 3 and 4, all exhibit negative plain curves in the region above 250 mμ, but the

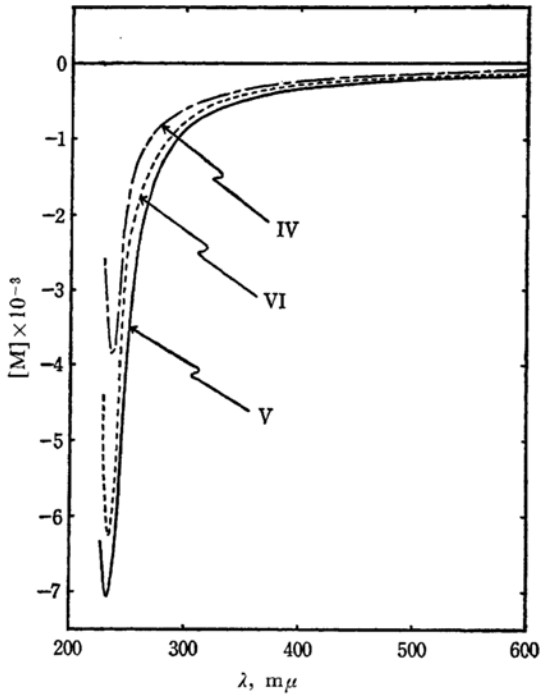


Fig. 3. RD of methylbenzylidene derivatives of diethyl tartrate.

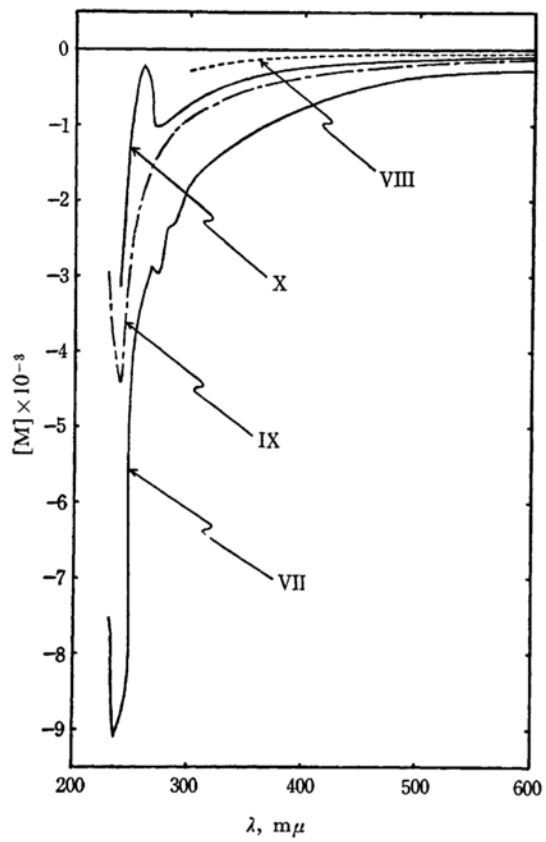


Fig. 4. RD of *o*- and *p*-halogenobenzylidene derivatives of diethyl tartrate.

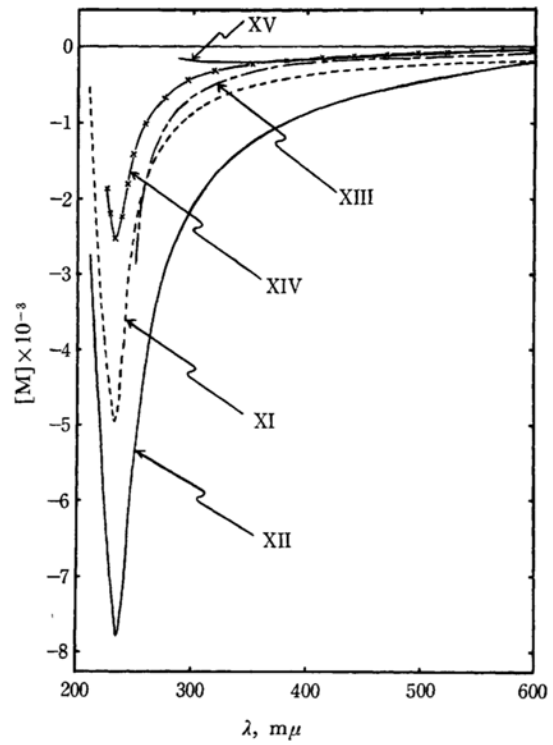


Fig. 5. RD of compounds XI—XV.

troughs appearing near 235 mμ are seen to show negative Cotton effects due to the carboxylate group.

In Fig. 5 are given the RD curves of the methylidene (XI), ethylidene (XII), vinylidene (XIII), benzylidene (XIV) and α-naphthylidene (XV) derivatives. These compounds exhibit negative plain curves in the region above 250 mμ and negative Cotton effects with troughs (near 235 mμ) similar in character to those shown in Figs. 3 and 4.

The RD curve of the compound XVI is illustrated in Fig. 6 together with the RD curves (I) and (IV) reproduced for comparison. In spite of the presence of ortho-nitro group, the compound XVI does not exhibit any Cotton effect near 340 mμ and the RD curve (XVI) runs closely along the background curve (IV) in the region above 340 mμ.

Furthermore, in view of the extraordinary optical rotation of *o*-nitrobenzylidene derivative (I), the conformation of the acetal ring was investigated by means of NMR spectrum. In the cases of $R \neq R'$, as may be seen in Fig. 7, the protons H_A and H_B are different in chemical environment, so that they interact to give a spin-spin coupling. From the coupling constant J_{AB}, as well as from Shimizu equation,[9]

$$J_{AB} = C + A|\cos\theta|,$$

9) H. Shimizu, "High Resolution Nuclear Magnetic Resonace," Maruzen, Tokyo (1962), p. 70.

where $C=0$ and $A=6.5+$ 1.5 cps in these cases, the angles, θ, of H_A–C–C–H_B can be calculated. The results are given in Table 1.

As may be seen in Table 1, the angles, θ, of the compounds are all in fairly good accordance with each other except for XVI. In other words, the stable conformations of the acetal rings of these compounds are nearly identical, where the two carboxylate groups of the tartrate are of the trans-form, and the acetal rings are, in all cases, of the half-chair form.

These compounds show in general negative rotations over all the wavelength range (Figs. 2, 3, 4, 5 and 6) but for the compound I. The fact that the angle, θ, of the compound XVI is considerably smaller than those of the others may be explained in terms of steric hindrance. It is thus

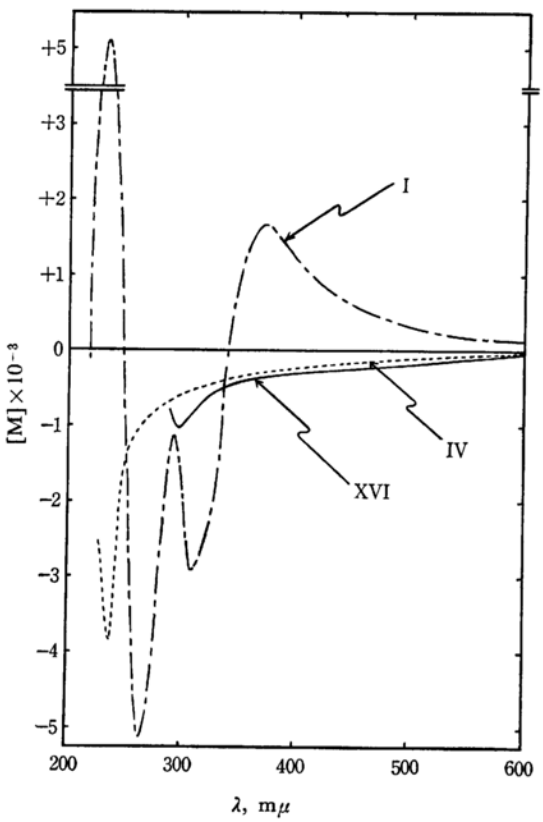


Fig. 6. RD of benzylidene derivatives of diethyl tartrate.

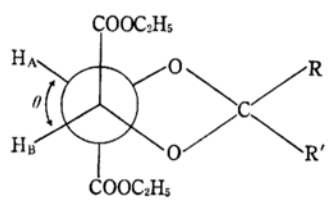


Fig. 7.

Table 1. NMR Data of the derivatives of ethyl *d*-tartrate at 25°C in CCl_4

Compound	Chemical shift of H_{AB}, ppm (δ)	J_{AB}-value, cps	θ
I	4.81	3.7	56°
II	4.83	3.9	54°
III	4.80	3.6	57°
IV	4.70	4.0	53°
V	4.71	3.8	55°
VI	4.70	3.8	55°
VII	4.77	3.6	57°
VIII	4.72	3.9	54°
IX	4.77	3.9	54°
X	4.71	4.3	48°
XII	4.51	3.9	54°
XIII	4.63	3.5	57°
XIV	4.76	3.9	54°
XV	8.88	3.8	58°
XVI	4.65	5.0	39°

concluded that the anomalous rotation of the *o*-nitrobenzylidene derivative (I) is not due to the distortion of the acetal ring that may be produced by the steric hindrance by the *o*-nitro group. It is, therefore, better to attribute this anomalous rotation to the property of the *o*-nitrophenyl group itself (Fig. 5).

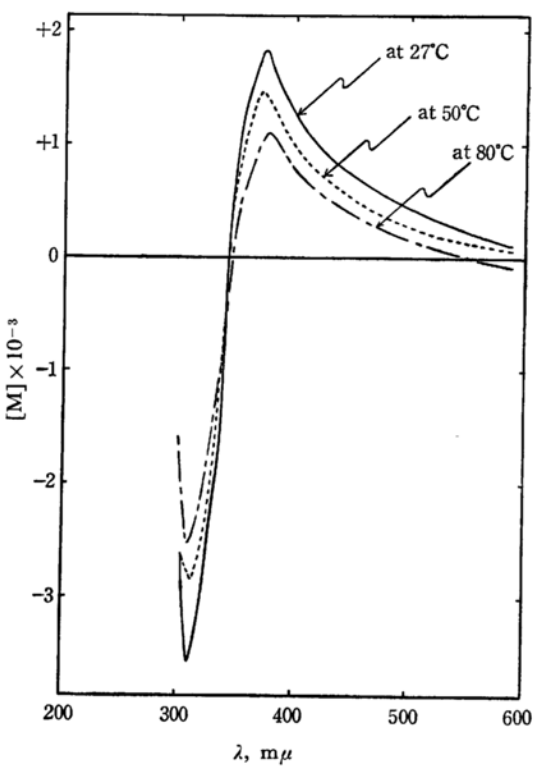


Fig. 8. Temperature variation of RD of I (in dimethyl formamide).

In addition, the authors have observed that the optical rotation of *o*-nitrobenzylidene derivative (I) varies with temperature: $[\alpha]_D^{27}$ +30.7°, $[\alpha]_D^{50}$ +20.9° and $[\alpha]_D^{80}$ −21.5° in dimethyl formamide, and with the increase of temperature the optical rotation tends to approach those of the *m*- or *p*-nitrobenzylidene derivatives, and have further noticed that the molecular amplitude of the Cotton effect near 340 mμ also diminishes with rise of temperature. The RD curves measured at 27, 50 and 80°C, of the compound I are shown in Fig. 8.

In view of these facts the ortho-nitro group must be twisted from the plane of the benzene ring by the steric hindrance of the bulky acetal ring, which may, on the other hand, be understood from the decrease of the strength of the UV absorption spectra. These can be regarded as charge transfer bands in view of Nagakura's report,[10] as is seen in Fig. 9; the compounds I and XVI each with a nitro group in the ortho-position of the phenyl group show $\varepsilon = 4.8 \times 10^3$ at 254 mμ and a shoulder at 243.6 mμ respectively, while the compounds II and III with a nitro group in the meta- and para-position show respectively $\varepsilon = 9.4 \times 10^3$ at 258.2 mμ and $\varepsilon = 10.2 \times 10^3$ at 260 mμ.

As may be seen in Fig. 6, the compound I could be measured down to 220 mμ, where the strong negative Cotton effect near 248 mμ appears to be due to the above-mentioned charge transfer band. In reality the UV spectra of the nitrobenzylidene derivatives have slight shoulders at 325—350 mμ due to the n–π^* transition that occurs possibly in the nitro group (Fig. 9). In the case of the compound I, this chromophore becomes optically active, but the compound XVI, in spite of its ortho-nitro group, does not exhibit any Cotton effect near 340 mμ. Furthermore, its UV absorption near 250 mμ is also very slight. However, the RD curve (XVI) also shows a Cotton effect near 290 mμ similar to the RD curve (I), although the former is very weak (see Fig. 6).

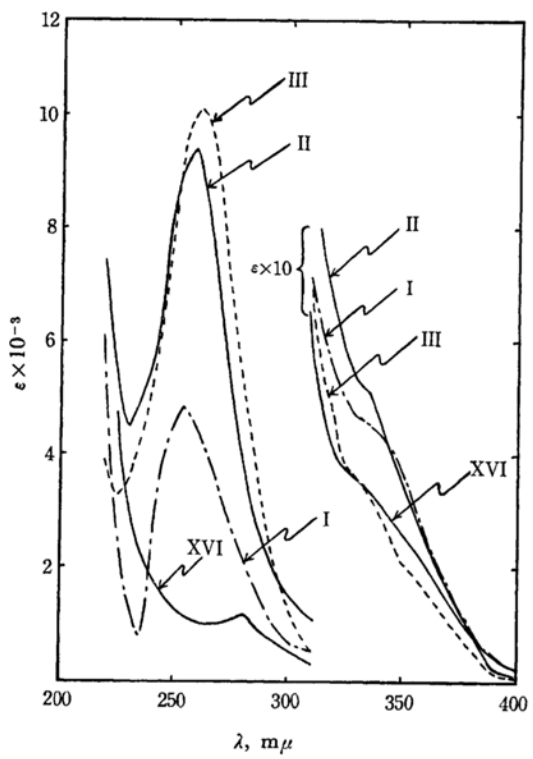


Fig. 9. UV spectra of nitrobenzylidene derivatives of diethyl tartrate.

According to the measurement and discussion by Nagakura *et al.*[10] of the absorption spectrum of nitromesitylene, the nitro group is twisted by 66.4° from the benzene ring plane and, accordingly, the conjugation between the mesityl and nitro groups must be prohibited to a great extent. Thus it is expected that the nitro group is in a similar manner twisted by about 30° in the *o*-nitrobenzylidene derivative (I) and by more than 66° in the 2-nitro-3,6-dimethylbenzylidene derivative (XVI).

These facts and considerations may lead to the conclusion that the anomalous positive rotation observed only in the *o*-nitrobenzylidene derivative is caused by its intense positive Cotton effect centered at 340 mμ, which dominates the positive sign of rotation further in the visible, and even if a nitro group is introduced in the ortho position, the nitro group cannot necessarily become optically active, as is seen in the compound XVI, which exhibit no anomalous rotation.

However, another important factor which induces the optical activity of the ortho-nitro group is to be sought for in the conjugation between the phenyl and nitro groups. The appearance of the Cotton effect at 260 mμ due to the charge transfer band shows that the *o*-nitro group is twisted unsymmetrically from the benzene ring plane under the influence of the unsymmetrical acetal ring, and the fact that molecular amplitude of the Cotton effect centered at 340 mμ distinctly decreases with rise of temperature may be interpreted in terms of the decrease of the unsymmetry of the twisted nitro group.

Anyhow, it must be admitted that further study will be needed to make clear the cause of the anomaly in rotation.

Experimental

The samples were all prepared according to the method described in the literature[11,12] at temperatures from 80 to 120°C. They were purified by recrystallization several times from ethyl alcohol or ethyl

10) S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spectry.*, **13**, 174 (1964).

11) Y. Tsuzuki, This Bulletin, **14**, 35 (1939).
12) Y. Tsuzuki, *ibid.*, **11**, 362 (1936).

alcohol-water, or by distillation in vacuum.

The rotatory dispersion was measured in ethyl alcohol at the temperatures 22 to 25°C in the wavelength region from 210 to 600 mμ with a Rudolph spectropolarimeter and JASCO optical rotatory dispersion recorder of the ORD/UV-5 type, and the circular dichroism was measured with the latter instrument. The NMR spectra were measured in carbon tetrachloride with tetramethylsilane as an internal reference with a Varian A-60 spectrometer. The ultraviolet absorption was measured in ethyl alcohol with a self-recording spectrophotometer of Hitachi EPU-II type.

Diethyl *o*-Nitrobenzylidene-*d*-tartrate (Compound I).[11] Colorless needles; mp 60°C. The RD was measured at 25°C in ethanol (*c* 0.701). $[\alpha]_{600}$ +38.3°, $[\alpha]_{589}$ +40.1°, $[\alpha]_{372}$ +493° (peak), $[\alpha]_{310}$ −879° (trough), $[\alpha]_{292}$ −324° (peak), $[\alpha]_{265}$ −1520° (trough), $[\alpha]_{231}$ +5120° (peak), $[\alpha]_{220}$ −914°. The RD by temperature variation of I was measured at 27, 50 and 80°C in dimethyl formamide and the concentrations were corrected, but the temperature dependence of the polarity of the solvent was ignored. $[\alpha]^{27}_{589}$ +30.7°, $[\alpha]_{500}$ +123°, $[\alpha]_{400}$ +368°, $[\alpha]_{375}$ +521° (peak), $[\alpha]_{310}$ −1050° (trough), $[\alpha]_{305}$ −777° (*c* 0.0978); $[\alpha]^{50}_{589}$ +20.9°, $[\alpha]_{500}$ +62.6°, $[\alpha]_{400}$ +282°, $[\alpha]_{370}$ +428° (peak), $[\alpha]_{310}$ −824° (trough), $[\alpha]_{305}$ −792° (*c* 0.0959); $[\alpha]^{80}_{589}$ −21.5°, $[\alpha]_{500}$ +43.0°, $[\alpha]_{400}$ +226°, $[\alpha]_{380}$ +333° (peak), $[\alpha]_{310}$ −742° (trough), $[\alpha]_{300}$ −473° (*c* 0.0930). The CD was measured at 25°C in ethanol (*c* 0.1301). $[\theta]_{410}$ +0°, $[\theta]_{330}$ −2890°, $[\theta]_{300}$ +832°, $[\theta]_{280}$ +2730°, $[\theta]_{250}$ −1900°, $[\theta]_{245}$ −1246°, $[\theta]_{235}$ −1724°, $[\theta]_{225}$ 0°.

Diethyl *m*-Nitrobenzylidene-*d*-tartrate (Compound II).[11] Colorless needles; mp 42—43°C. The RD was measured at 23°C (*c* 0.497). $[\alpha]_{600}$ −34.2°, $[\alpha]_{589}$ −35.6°, $[\alpha]_{400}$ −88.8°, $[\alpha]_{350}$ −142°, $[\alpha]_{310}$ −2110°.

Diethyl *p*-Nitrobenzylidene-*d*-tartrate (Compound III).[11] Pale yellow needles; mp 57—58°C. The RD was measured at 23°C (*c* 0.496). $[\alpha]_{600}$ −21.7°, $[\alpha]_{589}$ −22.3°, $[\alpha]_{400}$ −43.7°, $[\alpha]_{350}$ −30.9°, $[\alpha]_{234}$ −69.3°.

Diethyl 2,5-Dimethylbenzylidene-*d*-tartrate (Compound IV). Colorless crystals; bp 183—184°C/3 mmHg. The RD was measured at 23°C (*c* 0.505). $[\alpha]_{600}$ −30.3°, $[\alpha]_{589}$ −31.3°, $[\alpha]_{400}$ −83.2°, $[\alpha]_{350}$ −122°, $[\alpha]_{300}$ −200°, $[\alpha]_{236}$ −1800° (trough), $[\alpha]_{230}$ −1430°.

Diethyl *m*-Methylbenzylidene-*d*-tartrate (Compound V). Pale yellow liquid; bp 165—166°C/3 mmHg. The RD was measured at 23°C (*c* 0.598). $[\alpha]_{600}$ −42.1°, $[\alpha]_{589}$ −43.0°, $[\alpha]_{400}$ −104°, $[\alpha]_{300}$ −273°, $[\alpha]_{234}$ −2280° (trough), $[\alpha]_{223}$ −2060°.

Diethyl *p*-Methylbenzylidene-*d*-tartrate (Compound VI). Pale yellow liquid; bp 189.5—190°C/5 mmHg. The RD was measured at 23°C (*c* 0.497). $[\alpha]_{600}$ −38.8°, $[\alpha]_{589}$ −39.5°, $[\alpha]_{400}$ −94.2°, $[\alpha]_{300}$ −225°, $[\alpha]_{234}$ −2010° (trough), $[\alpha]_{230}$ −1420°.

Diethyl *o*-Iodobenzylidene-*d*-tartrate (Compound VII). Colorless needles; mp 34°C. The RD was measured at 23°C (*c* 0.503). $[\alpha]_{600}$ −65.7°, $[\alpha]_{589}$ −65.7°, $[\alpha]_{400}$ −180°, $[\alpha]_{280}$ −567°, $[\alpha]_{272}$ −707° (trough), $[\alpha]_{266}$ −697°, $[\alpha]_{236}$ −2160° (trough), $[\alpha]_{232}$ −1790°.

Diethyl *p*-Iodobenzylidene-*d*-tartrate (Compound VIII). Pale yellow liquid; bp 198°C/6 mmHg. The RD was measured at 22°C (*c* 0.708). $[\alpha]_{589}$ −4.93°, $[\alpha]_{400}$ −15.0°, $[\alpha]_{350}$ −26.9°, $[\alpha]_{300}$ −61.1°.

Diethyl *o*-Chlorobenzylidene-*d*-tartrate (Compound IX).[11] Colorless needles; mp 34—35°C. The RD was measured at 22°C (*c* 0.514). $[\alpha]_{589}$ −39.0°, $[\alpha]_{400}$ −106°, $[\alpha]_{300}$ −269°, $[\alpha]_{235}$ −1430° (trough), $[\alpha]_{230}$ −902°.

Diethyl *p*-Chlorobenzylidene-*d*-tartrate (Compound X).[11] Pale yellow liquid; bp 186—187°C/4 mmHg. The RD was measured at 22°C (*c* 0.519). $[\alpha]_{589}$ −26.7°, $[\alpha]_{400}$ −70.7°, $[\alpha]_{280}$ −314° (trough), $[\alpha]_{255}$ −103°, $[\alpha]_{240}$ −95.4°.

Diethyl Methylidene-*d*-tartrate (Compound XI).[12] Colorless liquid; bp 120—122°C/12 mmHg. The RD was measured at 23°C (*c* 0.577). $[\alpha]_{600}$ −77.5°, $[\alpha]_{589}$ −78.4°, $[\alpha]_{400}$ −112°, $[\alpha]_{300}$ −248°, $[\alpha]_{232}$ −2270° (trough), $[\alpha]_{210}$ −244°.

Diethyl Ethylidene-*d*-tartrate (Compound XII).[12] Colorless liquid; bp 132—134°C/17 mmHg. The RD was measured at 23°C (*c* 0.544). $[\alpha]_{600}$ −72.4°, $[\alpha]_{589}$ −74.6°, $[\alpha]_{400}$ −139°, $[\alpha]_{300}$ −388°, $[\alpha]_{264}$ −3340° (trough), $[\alpha]_{210}$ −1170°.

Diethyl Vinylidene-*d*-tartrate (Compound XIII). Colorless liquid; bp 169°C/36 mmHg. The RD was measured at 23°C (*c* 0.568). $[\alpha]_{589}$ −29.9°, $[\alpha]_{400}$ −83.6°, $[\alpha]_{300}$ −246°, $[\alpha]_{250}$ −1230°.

Diethyl Benzylidene-*d*-tartrate (Compound XIV). Colorless prisms; mp 48—49°C. The RD was measured at 23°C (*c* 0.703). $[\alpha]_{600}$ −18.0°, $[\alpha]_{589}$ −19.2°, $[\alpha]_{400}$ −52.4°, $[\alpha]_{300}$ −129°, $[\alpha]_{232}$ −866°, $[\alpha]_{227}$ −606°.

Diethyl α-Naphthylidene-*d*-tartrate (Compound XV). Colorless needles; mp 63—64°C. The RD was measured at 22°C (*c* 0.498). $[\alpha]_{589}$ −19.3°, $[\alpha]_{450}$ −37.2°, $[\alpha]_{345}$ −54.1° (trough), $[\alpha]_{290}$ −39.0°.

Diethyl 2-Nitro-3,6-dimethylbenzylidene-*d*-tartrate (Compound XVI). Pale yellow needles; mp 46.5—47.5°C. The RD was measured at 23°C (*c* 0.507). $[\alpha]_{600}$ −26.0°, $[\alpha]_{589}$ −28.9°, $[\alpha]_{450}$ −56.7°, $[\alpha]_{350}$ −107°, $[\alpha]_{298}$ −291° (trough), $[\alpha]_{290}$ −234°.

The authors owe the Ministry of Education a grant.