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THE TWO DIASTEREOMERS OF [3](2,5)(7,7,8,8-TETRACYANOQUINODIMETHANO)-[3](2,5-DIMETHOXYPARACYCLOPHANE) [1)]

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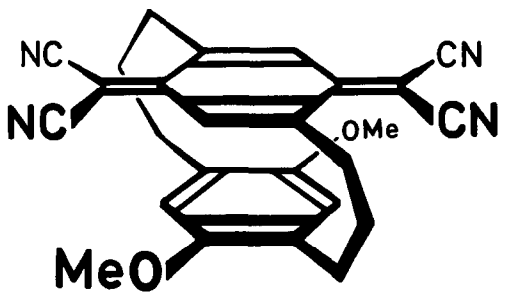
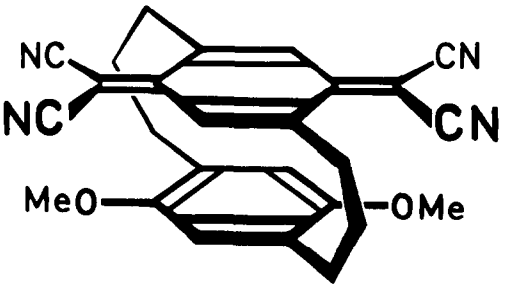
As the first set of stereomeric donor-acceptor cyclophanes with TCNQ as an acceptor, 1 and 2 were synthesized; their charge-transfer absorptions differ strongly as a consequence of the different donor-acceptor orientation.

Recently, as a donor-acceptor cyclophane with tetracyanoquinodimethane (TCNQ) as the acceptor component, [2](2,5)(7,7,8,8-tetracyanoquinodimethano)-[2](2,5-dimethoxyparacyclophane) was prepared [2)]. The synthesis of the same compound, together with some multi-layered analogues, was somewhat later reported also by Misumi and his group [3)]. In both studies, however, only the more easily accessible pseudoortho compound of the two possible stereomers was obtained. Yet, in the context of our work on orientation dependence of charge-transfer (CT) interactions, the comparison of the CT properties of the pseudoortho and the pseudogeminal stereomers was required. Recent results in the quinhydrone series showed that, for such comparisons, donor-acceptor [3.3]paracyclophanes due to considerably less sterical deformations and nearly normal donor-acceptor distances are more appropriate models to simulate intermolecular CT interactions than their analogues of the [2.2] series [4)]. We therefore decided to synthesize [3](2,5)(7,7,8,8-tetracyanoquinodimethano)-[3](2,5-dimethoxyparacyclophanes) the preparation of the two stereomers of which, the pseudoortho compound 1 and the pseudogeminal isomer 2, is reported here.



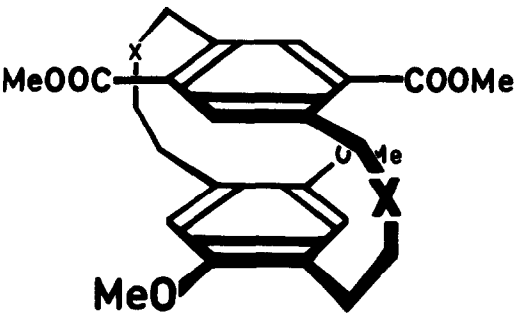
1

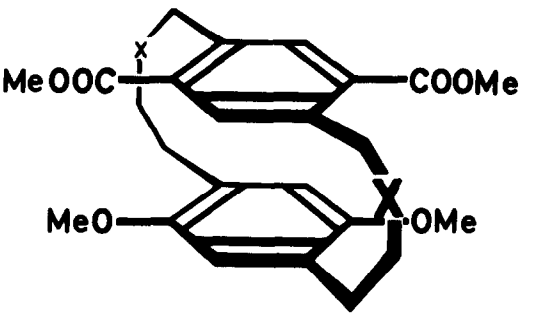


2

For the synthesis of 1 and 2, dimethyl 2,5-bis(bromomethyl)terephthalate and 1,4-bis(1-mercaptoethyl)-2,5-dimethoxybenzene were cyclized [slow addition

of the solution of the reactants in methanol/tetrahydrofuran (1:1) to potassium carbonate in boiling methanol]. The 16,19-bis(carbomethoxy)-6,9-dimethoxy-2,13-dithia[4.4]paracyclophanes were formed (41 % yield) as a 4:3 mixture of pseudoortho and pseudogeminal stereomers (3 and 4, resp.) the separation of which was easily possible on the basis of the good solubility of 3 in acetone: 3 [5]: m.p. 244 - 245° C; ^{1}H-NMR (80 MHz, $CDCl_3$): δ = 1.8 - 3.6 (m, 8 H), 3.69 (s, 6 H), 3.91 (s, 6 H), 3.55/4.06 (AB, J = 14 Hz, 4 H), 6.33 (s, 2 H), 7.36 (s, 2 H); 4 [5]: m.p. 186 - 188° C; ^{1}H-NMR (80 MHz, $CDCl_3$): δ = 1.8 - 3.7 (m, 8 H), 3.63 (s, 6 H), 3.90 (s, 6 H), 3.25/4.72 (AB, J = 14.6 Hz, 4 H), 6.34 (s, 2 H), 7.66 (s, 2 H). Oxidation of 3 (m-chloroperbenzoic acid, chloroform, 20° C) resulted in the formation of the disulfone 5 [5] (m.p. 264 - 266° C, 75 % yield); from 4 under similar conditions 6 [5] was obtained (m.p. 335 - 340° C, dec.; 93 % yield).





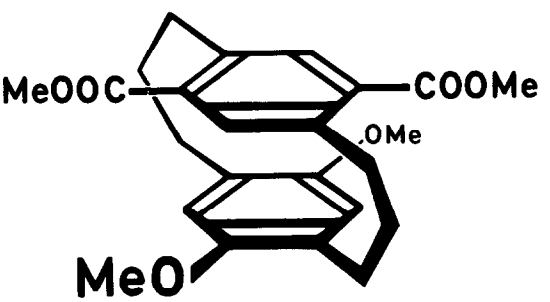
3: X = S
5: X = SO_2

4: X = S
6: X = SO_2

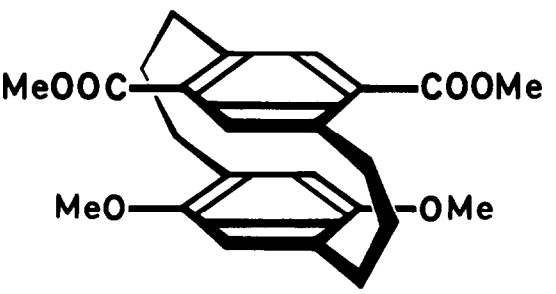
Vapour phase pyrolysis of the disulfones 5/6 (580° C, 0.001 Torr) resulted in the formation of the carbocyclic [3.3]paracyclophanes (43 % yield) which by fractional crystallization from n-hexane were separated into the pseudoortho and pseudogeminal isomers 7 and 8 (ratio 2:1). 7 [5]: yellow crystals, m.p. 77 - 78° C; ^{1}H-NMR (80 MHz, $CDCl_3$): δ = 1.75 - 4.25 (m, 12 H), 3.74 (s, 6 H), 3.91 (s, 6 H), 6.23 (s, 2 H), 7.54 (s, 2 H); 8 [5]: yellow crystals, m.p. 170 - 171° C; ^{1}H-NMR (80 MHz, $CDCl_3$): δ = 1.75 - 4.20 (m, 12 H), 3.65 (s, 6 H), 3.91 (s, 6 H), 6.16 (s, 2 H), 7.50 (s, 2 H). As the preceding very similar ^{1}H-NMR data show, the assignment of these stereomeric [3.3]paracyclophanes 7 and 8, in contrast to most diastereomers of the [2.2]paracyclophane series, cannot be derived from ^{1}H-NMR data. For the assignment given for 7 and 8 we have less stringent evidence based on empirical rules (ratios of yields, melting points, solubilities etc.) which were shown to hold for a large number of pairs of stereomeric [2.2]- and [3.3]paracyclophanes. Nevertheless, the assignment to 7 and 8 remains to be checked by X-ray analysis.

Reduction of 7 and 8 (lithiumaluminium hydride, tetrahydrofuran, 6 h, reflux) yielded the corresponding 5,8-bis(hydroxymethyl) compounds 9 [5] (m.p.

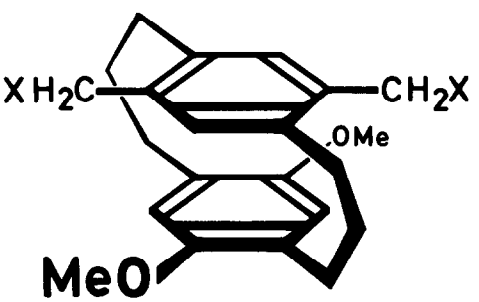
129 - 130° C; 88 % yield) and 10 [5] (m.p. 189 - 190° C; 89 %). With PBr_3/toluene from 9 the bis(bromomethyl) compound 11 [5] (m.p. 128 - 129° C, 89 % yield) and from 10 under the same conditions 12 [5] (m.p. 172 - 173° C, 88 % yield) were obtained. Reaction with sodium cyanide in dimethylsulfoxide (30 min, 60° C) converted 11 into 13 [5] (m.p. 228 - 229° C, 84 % yield); under similar conditions (45 min, 80° C) 12 yielded 14 [5] (m.p. 163 - 164° C, 81 % yield).



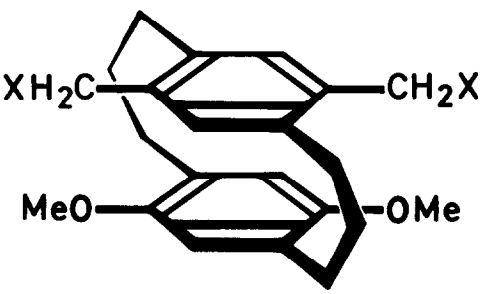
7



8



9: X = OH
11: X = Br
13: X = CN



10: X = OH
12: X = Br
14: X = CN

After dimethyl carbonate condensation of 13 (excess potassium-tert.-butoxide, under nitrogen, gradually increasing temperature to reflux, 3 h), evaporation under vacuum and addition of toluene to the residue, cyanogen chloride was introduced (0° C ⟶ 60° C, 2 h) [6]. Following destillation under vacuum the solid residue was hydrolyzed with 25 % aqueous potassium hydroxide, acidified and the precipitate oxidized with silver oxide (acetone, 20° C). Chromatography on silica from dichloromethane and recrystallization from acetonitrile gave pure 1 [5] in 20 % yield. 1: dark-red (almost black) microcrystals, dec. > 280° C; ^{1}H-NMR (80 MHz, $CDCl_3$): δ = 1.85 - 3.62 (m, 12 H), 3.79 (s, 6 H), 6.33 (s, 2 H), 6.91 (br. s, 2 H).

Essentially the same procedure converted 14 into 2 [5] (11 % yield) which was recrystallized from acetonitrile: black microcrystals, dec. > 250° C; ^{1}H-NMR (80 MHz, $CDCl_3$): δ = 1.75 - 3.75 (m, 12 H), 3.78 (s, 6 H), 6.25 (s, 2 H), 6.61 (d, J = 1.6 Hz, 2 H).

Whereas all other spectroscopic data for 1 and 2 (^{1}H-NMR, MS, IR) are very similar there is a very strong intensity difference of the CT absorptions which for both compounds extend from about 550 up to 1000 nm (Fig.): the molar extinction coefficient ε for 1 (λ_{max} = 670 nm) is 117, that for 2 (λ_{max} = 705 nm) is 3452. Thus, the strong orientation dependence derived for the quinhydrone series is also observed for TCNQ-containing CT systems. The implications of this finding regarding semi- and photoconductivity of TCNQ-donor-systems will be further studied [7].

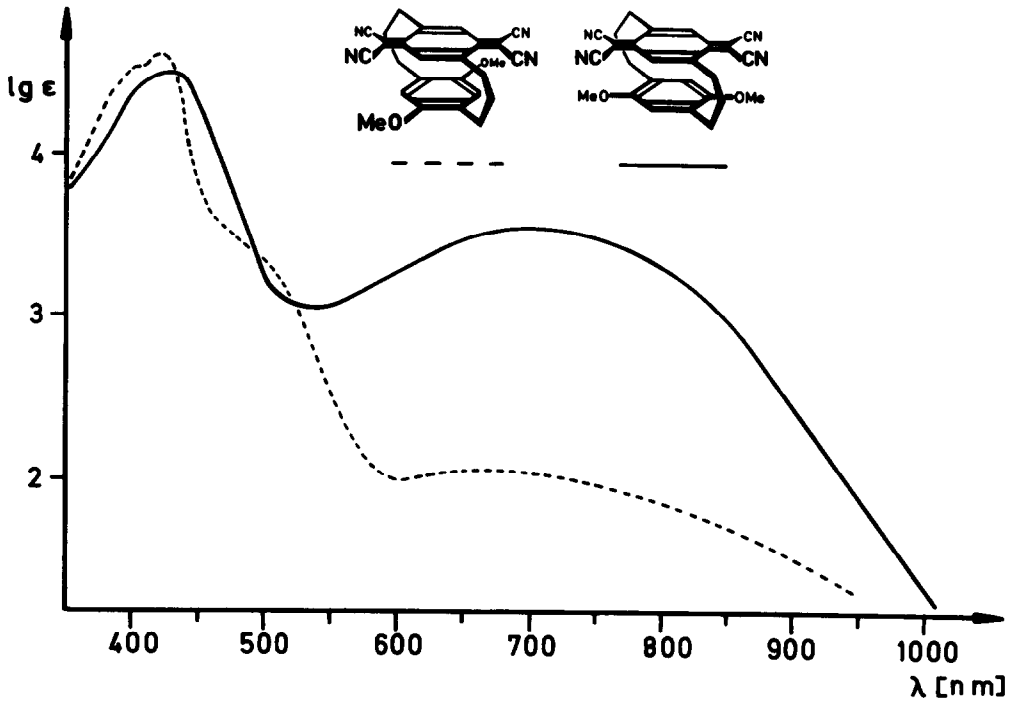


Fig. CT-Absorptions of 1 and 2 (in chloroform)

1) Electron-Donor-Acceptor Compounds Part 27. - Part 26: J. Ippen, Chu Tao-pen, B. Starker, D. Schweitzer and H. A. Staab, Angew. Chem. (in press).

2) H. A. Staab and H.-E. Henke, Tetrahedron Lett. 1978, 1955; cf. H. A. Staab, Lecture ISNA III San Francisco, Calif. August 22, 1977.

3) H. Tatemitsu, B. Natsume, M. Yoshida, Y. Sakata and S. Misumi, Tetrahedron Lett. 1978, 3459.

4) H. A. Staab and C. P. Herz, Angew. Chem. 89, 839 (1977); Angew. Chem. Int. Ed. Engl. 16, 799 (1977).

5) Elementary analyses, molecular weights and spectroscopic properties are in agreement with the postulated structures.

6) With the procedure applied here for 1 and 2 the synthesis of the formerly prepared 1-analogue of the [2.2]paracyclophane series [2] was improved in the overall yield from the bis(cyanomethyl) step to the TCNQ phane from 1 to 34 %.

7) Preliminary conductivity measurements of pellets of crystal powder of the TCNQ cyclophanes reported in this paper showed values in the lower semiconductor range: D. Schweitzer, to be published.

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