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2,4-DICHLORO-3-(DIMETHYLAMINOMETHYLENE)-1,4-CYCLOHEXADIENE-1,5-DICARBOXALDEHYDE: X-RAY STRUCTURE, MNDO CALCULATIONS, AND ROTATIONAL BARRIERS OF A STABLE NON-AROMATIC TAUTOMER OF A PENTA-SUBSTITUTED BENZENE

By Alan R. Katritzky*, Charles M. Marson, Gus Palenik, Anna E. Koziol,
Hudson Luce, Mati Karelson, Ban-Chi Chen, and Wallace Brey
Department of Chemistry, University of Florida, Gainesville, FL 32611, USA

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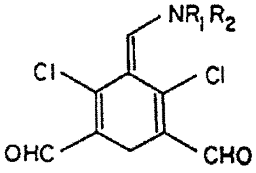
Abstract -- Analogues of the title compound have been prepared; minor alterations in the reaction conditions give a benzenoid isomer 2b of the title compound. Reactions of the title compound were studied, and the structure was confirmed by X-ray crystallography. MNDO calculations give a geometry in agreement with that found, and indicate an energy difference of 13 kcal/mol in favour of the benzenoid isomer 2a. Temperature-dependent ^{13}C- and ^{1}H-NMR spectra afforded rotational barriers.

The isolation of 2,4-dichloro-3-(N,N-dimethylaminomethylene)-1,4-cyclohexadiene-1,5-dicarboxaldehyde 1a, obtained by the action of the iminium salt from DMF/$POCl_3$ on cyclohexane-1,3-dione at 20 °C, was recently reported.[1] Dialdehyde 1a is stable at 20 °C for at least several weeks. In view of the resonance energy of benzene, ca. 36 kcal mol^{-1},[1,2] it seemed remarkable that dialdehyde 1a could exist without conversion into the benzenoid tautomer 2a; for this reason we have continued our investigations.

In the present paper we report: (i) further preparative work including the synthesis and some transformations of analogues of dialdehyde 1a, (ii) conclusive proof of the structure by X-ray analysis, (iii) MNDO calculations of the energy of compounds of this type and of their benzenoid tautomers, (iv) measured rotational barriers in compound 1a.

PREPARATION OF CHLORINATED ALDEHYDES

Reaction of cyclohexane-1,3-dione at 20 °C with iminium salts derived from mixtures of $POCl_3$ with N-methylformanilide, pyrrolidine-N-carboxaldehyde and N-formylmorpholine afforded the novel 1,4-cyclohexadiene-1,5-dicarboxaldehydes 1b, 1c and 1d, respectively. With a variety of dialdehydes 1 in hand, attempts were made to prepare the benzenoid tautomers (e.g. dialdehyde 2a; vide infra). During the preparation of dialdehydes 1, none of the corresponding benzenoid tautomers was detected. However, we have now found that dialdehyde 2b can be obtained by performing the above reaction with dimethylformamide at 100 °C. At that temperature, no dialdehyde 1a was detected. The ^{1}H-NMR spectrum of dialdehyde 2b displayed signals at delta 3.63 (CH_2) and 8.20 (CH), signals at chemical shifts appreciably different from the methylene and methine resonances[1] of dialdehyde 1a, at delta 3.27 and 7.61, respectively. The ^{13}C NMR spectrum of dialdehyde 2b displayed signals for CH_2 at 59.2 ppm and for CH at 132.7 ppm; again, the corresponding signals for dialdehyde 1a occur[1] at 23.3 and 151.3 ppm. Neither the spectrum of dialdehyde 1a nor that of dialdehyde 2b disclosed signals due to the other isomer.



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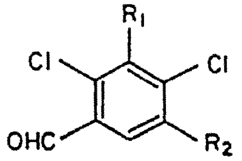

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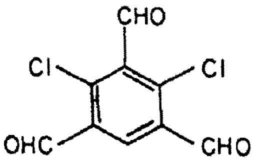

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a $R_1=R_2=Me$ b $R_1=Me,R_2=Ph$ a $R_1=CH_2NMe_2$; $R_2=CHO$
c $R_1,R_2=(CH_2)_4$ d $R_1,R_2=(CH_2)_2O$ b $R_1=CHO$; $R_2=CH_2NMe_2$

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* This paper is dedicated to Ted Taylor on his 65th birthday, wishing him many more!

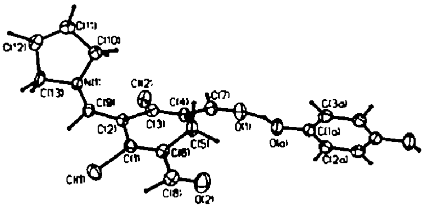
In attempts to convert dialdehyde 1a into the benzenoid tautomer 2a, the former was subjected to a variety of conditions and reagents. Heating dialdehyde 1a at 150 °C under argon afforded a tarry residue mainly insoluble in $CHCl_3$ and from which neither dialdehyde 1a nor dialdehyde 2a could be obtained. Heating a solution of dialdehyde 1a in $POCl_3$ under reflux in a stream of argon afforded an oil which also contained neither dialdehyde 1a nor dialdehyde 2a; products of hydrolysis of the beta-chlorovinylaldehyde moieties in dialdehyde 1a appeared to be formed. Reaction of the latter with $AlCl_3$ (3 mol) in CH_2Cl_2 at 20 °C also gave hydrolysis products which could not be readily identified. When dialdehyde 1a was added to conc. H_2SO_4 at 20 °C a deep purple solution resulted. Although ESR indicated the presence of radicals, no data could be obtained .

The action of methanolic NaOMe caused decomposition of dialdehyde 1a, apparently involving displacement of Cl^-; the products could not be identified. The action of $BF_3.Et_2O$ in CH_2Cl_2 upon dialdehyde 1a at 20 °C afforded the trialdehyde 3 in 17 % yield. It seems likely that trialdehyde 3 was produced by aerial oxidation of dialdehyde 1a, although the mechanistic details are not currently known. Interestingly, no carboxylic acids were detected in the mass spectra of any of the products isolated from the above reactions.

X-RAY CRYSTALLOGRAPHIC ANALYSIS

The structures of 1c and 4 (the 2:1 adduct of 1c with hydroquinone) were determined by X-ray diffraction. The adduct was discovered in a sample of 1c recrystallised from $i\text{-}Pr_2O$ containing hydroquinone as a stabiliser and was subsequently prepared by co-crystallising the two components from a mixture of $CHCl_3$ - EtOAc - petroleum. Crystals of 1c are triclinic, $P\bar{1}$ with a = 8.1939 (17), b = 9.1772 (19), c = 10.0050 (20) Å, alpha = 73.510 (17), beta = 108.512 (16), gamma = 114.704 (15)° and V = 638.06 (23) $Å^3$. D_m = 1.482 and D_x = 1.489 g cm^{-3} for Z = 2. A crystal 0.08 x 0.34 x 0.44 mm was used to measure 1675 reflections, of which 1458 with Fobs $\geq$ 3 sigma (Fobs) were used in the analysis. The final R = 0.035 and R_w = 0.031. Crystals of 4 are triclinic, $P\bar{1}$, a = 8.5692 (23), b = 9.0718 (24), c = 10.7684 (23) Å, alpha = 105.196 (18), beta = 91.706 (20), gamma = 105.494 (21)°, V = 774.0 (3) $Å^3$. The values D_m = 1.445 and D_x = 1.464 g cm^{-3} are for one 2:1 adduct per cell. A crystal 0.11 x 0.27 x 0.38 mm was used to measure 2139 reflections, of which 1829 with Fobs $\geq$ 3 sigma (Fobs) were used in the analysis. The final R = 0.045 and R_w = 0.035. Tables of the final positional parameters, thermal parameters, and bond angles have been submitted to the Cambridge Crystallographic Data Centre. All calculations on both compounds used the SHELXTL programs. Rev. 4.0, on a Model 30 Eclipse. All the measurements were made with a Nicolet R3m diffractometer, using graphite-monochromatised MoK-alpha radiation.

A drawing of the adduct 4 is given in Figure 1. The hydroquinone molecule lies on the crystallographic centre of symmetry and is hydrogen-bonded to O(1) of the aldehyde on the cyclohexadiene ring. Bond distances in 4 and 1c are compared in Table 1. The lengthening of C(7)-O(1) and the shortening of C(4)-C(7) bonds in 4, relative to 1c, are consequences of the presence of the hydrogen bond. All other distances in the cyclohexadiene portions of 4 and 1c are closely similar.



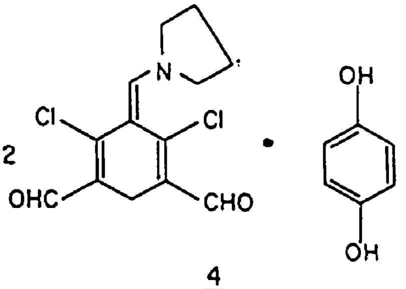


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Figure 1. The hydroquinone adduct 4 showing the thermal ellipsoids, atomic numbering and the O(1) - O(a) hydrogen bond.

Table 1. The MNDO optimised bond lengths, dipole moments and enthalpies of formation for 1a, 1c and 2a, and selected experimental X-ray bond lengths for 1c and 4.

Bond	MNDO Calculated Bond Lengths (Å)			X-Ray Bond Lengths	
(see Fig. 1 for numbering)	1c	1a	2a	1c	4
C(1) - C(2)	1.484	1.466	1.420	1.454(4)	1.462(3)
C(1) - C(6)	1.359	1.365	1.413	1.349(3)	1.341(4)
C(2) - C(3)	1.479	1.473	1.421	1.442(4)	1.440(4)
C(2) - C(9)	1.369	1.393	1.529	1.388(3)	1.389(4)
C(3) - C(4)	1.354	1.369	1.414	1.347(3)	1.352(4)
C(4) - C(5)	1.519	1.491	1.409	1.495(5)	1.500(4)
C(4) - C(7)	1.501	1.506	1.506	1.458(5)	1.427(5)
C(5) - C(6)	1.503	1.489	1.410	1.495(4)	1.504(4)
C(6) - C(8)	1.501	1.504	1.506	1.457(4)	1.448(4)
C(7) - O(1)	1.219	1.217	1.219	1.214(4)	1.233(4)
C(8) - O(2)	1.220	1.220	1.219	1.219(4)	1.222(4)
C(9) - N(1)	1.410	1.373	1.471	1.323(3)	1.317(3)
N(1) - C(10)	1.468	1.479	1.468	1.463(3)	1.476(4)
N(1) - C(13)	1.469	1.482	1.468	1.480(3)	1.483(4)
Dipole Moment	4.01	11.45	1.72	--	---
Delta H^{o}_{f} (kcal/mol)	-189.1	-26.3	-39.7	--	---

The average of the C(1)-C(6) and C(3)-C(4) distances in 1c is 1.348 Å, which clearly establishes the cyclohexadiene formulation. The average is slightly longer than the distance observed in three similar cyclohexadiene compounds: perchlorobenzylidenecyclohexa-2,5-diene,[2] and the solvated[3] and unsolvated[4] forms of 1-diphenylmethylene-4-triphenylmethylcyclohexa-2,5-diene. There appears to be some delocalisation between the C=C and the C=O groups which lengthens the former bond and shortens the latter bond.

The cyclohexadiene ring is in a boat conformation, atoms C(1), C(3), C(4), and C(6) being approximately planar. In 1c, 4, and perchlorobenzylidenecyclohexa-2,5-diene[2] the methylene carbon, C(5), is 0.208, 0.215 and 0.207 Å respectively above the plane, while the trigonal carbon, C(2), is 0.310, 0.326 and 0.329 Å respectively above the plane. Surprisingly, the cyclohexadiene ring in the solvated[3] and unsolvated forms[4] of the triphenylmethyl "dimer" is closer to planarity. Presumably, the steric interactions involving the phenyl rings can be relieved by flattening the cyclohexadiene ring. While there are no significant differences between the cyclohexadiene rings in 1c and 4, the solvated species 4 does appear to have larger differences in chemically equivalent bonds owing to hydrogen-bonding.

M.O. CALCULATIONS

Full geometry optimisations of the molecules 1a and 2a were carried out using the MNDO quantum-chemical method.[5] The calculated optimised bond lengths are recorded in Table 1. The experimental and theoretical bond lengths (and angles) are in good agreement with the non-benzenoid molecules 1a and 1c. The largest discrepancy is observed for the C(9)-N(1) bond length (about 0.09 Å). The other calculated and experimental lengths are equal, within 0.01-0.05 Å, the MNDO calculated values usually being larger.

The MNDO energy difference between the non-benzenoid compound 1a and its benzenoid isomer 2a predicts the latter to be more stable by about 13 kcal/mol (Table 1). That difference is markedly smaller than the usual value of the resonance energy of a substituted benzene ring (ca. 30 kcal/mol). An extra stabilisation energy of ca. 17 kcal/mol for 1a is implied, and is evidently caused by the extensive delocalisation of charge.

No such resonance interaction is possible in the case of the benzenoid molecule 2a. These differences in charge delocalisation of 1a and 2a result in a big difference of the dipole moment values of these molecules (Table 1). The Kirkwood-Onsager theory of dielectric solvation of the molecules[6] states that the dipolar stabilisation energy (ΔE_{el}) is proportional to the square of the dipole moment mu^2 of a given molecule in a condensed medium of dielectric permittivity epsilon (Eq. 1). Hence, depending on the value of cavity radius α_0 chosen for the molecule, the nonbenzenoid form 1a may even be more thermodynamically stable in solution than its tautomeric form 2a. Quantitative SCRF calculations[7,8] should give a good estimate of the difference of electrostatic solvation energy of these compounds in solution.

$$\Delta E_{el} = - (\varepsilon-1) / [\alpha_0^3(2\varepsilon+1)].\ \mu^2 \qquad \text{(Eq. 1)}$$

The experimentally observed high stability of the compound 1c with respect to the benzenoid form could also be due to kinetic factors. MNDO calculations show a marked lowering of the positive charge at the methylene hydrogen atoms of compound 1a. This implies stronger bonding between the annular carbon and the methylene hydrogen atoms of compound 1a, and ipso facto an elevated activation energy barrier for the isomerisation 1a ---> 2a. We are currently exploring the pathway by which cyclohexane-1,3-dione is converted into dialdehyde 2b, and we are seeking an explanation of why the latter is formed, rather than the isomer 2a.

TEMPERATURE-DEPENDENCE OF NMR SPECTRA

Fourier-transform carbon-13 spectra at 75 MHz and hydrogen spectra at 300 MHz were obtained for 1a at temperatures between -60°C and +55°C. Temperatures of the samples were controlled to 0.3°C by passing chilled or heated N_2 through the probe. Digital resolution was 0.35 Hz for the ^{13}C NMR spectra and 0.12 Hz for the ^1H NMR spectra.

The aim of this work was to evaluate the barriers to rotation for the groups attached to the cyclohexadiene ring. The two methyl groups of dialdehyde 1a show different chemical shifts at low temperatures in both ^1H and ^{13}C NMR spectra owing to the delocalisation of the formally unshared electron pair on nitrogen. At room temperature and above, the coalescence of these peaks was observed in both the ^1H and ^{13}C NMR spectra. Non-equivalence was also demonstrated at low temperatures in the ^{13}C NMR spectrum for ring carbon atoms 2 and 4, 1 and 5, and the two aldehydic carbons, as well as in the ^1H NMR spectrum for the two aldehydic hydrogens. At sufficiently high temperature, coalescence of all these pairs was observed, although at room temperature the ring carbon resonances were still somewhat broad.

From the observed coalescence temperature, T_c, and the limiting low temperature shift difference, δ, the free energy of activation for the rotational processes may be estimated from equation 2.[9] The results of these calculations are given in Table 2.

$$\Delta G^{\neq} = 4.576\ T_c\ [9.97 + \log T_c/\delta]\ \text{cal/mol} \qquad \text{(Eq. 2)}$$

Table 2. Barriers to Bond Rotation Determined from NMR Coalescence Temperatures

	Data from ^1H Spectra			Data from ^{13}C Spectran			
Atomic Group[a]	δ (Hz)	T_c (°K)	$\Delta G^{\neq}$ (kcal/mol)	δ(Hz)	T_c (°K)	$\Delta G^{\neq}$ (kcal/mol)	ΔE_a (kcal/mol)
CHO	4.8 ± 0.1	235 ± 2	12.5 ± 0.2	60 ± 3	229 ± 4	11.1 ± 0.5	---
1 and 3	---	---	-----	290 ± 5	258 ± 3	11.7 ± 0.4	7.8 ± 0.4
4 and 6	---	---	-----	290 ± 5	258 ± 3	11.7 ± 0.4	7.8 ± 0.4
NMe_2	41 ± 1	248 ± 5	12.2 ± 0.5	215 ± 5	271 ± 2	12.5 ± 0.5	13.5 ± 0.5

Attempts were made to evaluate the Arrhenius energy of activation (ΔE_a) from measurements of the NMR lineshapes below and above coalescence. In the ^1H NMR spectrum, the CH_2 resonance moves through the $-NMe_2$ resonance as the temperature changes; overlap prevented accurate evaluation of the shape of either resonance. Results of lineshape fitting for the aldehyde, ring, and NMe_2 carbon atoms, assuming two equally populated sites, are given in Table 2. Two distinct processes are expected to affect the spectral equivalence of various atoms: (i) Rapid rotation about the formal double bond $C=CHNMe_2$ should render equivalent the CHO groups, the 1,5-pair of ring carbons, and the 2,4-pair of ring carbons; (ii) rapid rotation about the formal single bond $CH-NMe_2$ should render equivalent the two methyl groups. The results (Table 2) indicate that these two processes must be very similar in energy. For process (i), four measurements of delta G are available with results of 11.1 - 12.5 kcal mol^{-1}. For process (ii) the two measurements indicate a barrier of ca. 12.2-12.5 kcal mol^{-1}. However, the temperature-dependence of the carbon lineshape for the aldehydic hydrogens does not follow a simple pattern, an indication that several processes may be contributing to the removal of nonequivalence of these groups.

EXPERIMENTAL

Melting points were taken on a Reichert hot stage apparatus and are uncorrected. ^1H NMR spectra were recorded with a Varian EM-360 spectrometer; ^{13}C NMR spectra (25.00 and 75.86 MHz) were recorded with XL-100 and Nicolet NT-300 spectrometers. IR spectra were measured on a Perkin Elmer 283-B spectrometer. Mass spectra were recorded on an AEI MS30 instrument. "Evaporation" refers to removal of solvent under reduced pressure. $MgSO_4$ was used as the drying agent.

General Procedure for Preparing Dialdehydes (1b), (1c), (1d). The appropriate formamide (15 ml) and phosphorus oxychloride (14.0 g, 0.091 mol) was stirred at 5 °C for 10 min and then allowed to stand at the ambient temperature for 10 min, followed by addition of cyclohexane-1,3-dione (3.36 g, 0.030 mol). The mixture was stirred at 20 °C for 72 h, then treated with CH_2Cl_2 (100 ml) and aqueous 10% Na_2CO_3 (100 ml); solid Na_2CO_3 was then added to bring the pH to 7.0. The organic layer was separated, washed with water (2 x 30 ml), dried and evaporated to give an oil which was treated as described below.

2,4-Dichloro-3-(N-methyl-N-phenylaminomethylene)-1,4-cyclohexadiene-1,5-dicarboxaldehyde (1b). The oil was chromatographed on silica gel (30g; 230-400 mesh) using ethyl acetate as the eluant (200 ml). Evaporation of the solvent and trituration of the residue with petroleum afforded 0.96 g (10 %) of 1b, which crystallised from chloroform as orange prisms, m.p. 128-130 °C; IR nu_{max} $CHBr_3$ 2920, 2860, 1655(s), 1585(s), 1530, 1270, 915, 855, 745 cm^{-1}; ^1H NMR ($CDCl_3$) delta 3.37 (2H, s),3.53 (3H, s), 7.00-7.40 (5H, m), 7.70 (1H, s), 10.07 (2H, s). Found: C, 59.75; H, 4.09; N, 4.31. Calc. for $C_{16}H_{13}Cl_2NO_2$: C, 59.65; H, 4.07; N, 4.35 %.

2,4-Dichloro-3-(pyrrolidinylmethylene)-1,4-cyclohexadiene-1,5-dicarboxaldehyde (1c). The oil was triturated with petroleum (3 x 20 ml; 60-80 °C), and then with diethyl ether (2 x 10 ml) to give 3.60 g (42%) of 1c, which crystallised from ethyl acetate as orange plates, m.p. 124-126 °C; IR nu_{max} $CHBr_3$ 2950 (w), 2870, 1650, 1580 (s), 1270, 920, 870 cm^{-1}; ^1H NMR ($CDCl_3$) delta 2.00 (4H, m), 3.27 (2H, s), 3.67 (4H, m), 7.63 (1H, s), 9.97 (2H, s); ^{13}C-NMR ($CDCl_3$) delta 23.4 (t), 24.7 (t), 54.9 (t), 148.0 (d), 188.1 (d). Found: C, 54.61; H, 4.60; N, 4.85. Calc. for $C_{13}H_{13}Cl_2NO_2$: C, 54.56; H, 4.58; N, 4.90%.

2,4-Dichloro-3-(morpholinylmethylene)-1,4-cyclohexadiene-1,5-dicarboxaldehyde (1d). The oil crystallised upon cooling to 0°C; the crystals were washed with diethyl ether (10 ml) to give 2.71 g (30%) of 1d which crystallised from acetic acid as orange prisms, m.p. 168-170 °C; IR nu_{max} $CHBr_3$ 2920(w), 2850, 1650, 1585(s), 1290(s), 1030, 910, 860 cm^{-1}; ^1H NMR ($CDCl_3$) delta 3.33 (2H, s), 3.75 (8H, m), 7.67 (1H, s), 10.27 (2H, s). Found: C, 51.58; H, 4.35; N, 4.64. Calc. for $C_{13}H_{13}NO_3$: C, 51.67; H, 4.34; N, 4.64%.

2,4-Dichloro-3-(N,N-dimethylaminomethyl)benzene-1,3-dialdehyde 2b. Cyclohexane-1,3-dione (3.36 g, 30 mmol) was added to a stirred mixture of dimethylformamide (5.6 g, 0.076 mol) and phosphorus oxychloride (11.7 g, 0.076 mol) in trichloroethylene (10 ml) at 5 °C. The ice bath was removed, chloroform (10 ml) added, and the mixture stirred at 20 °C for 30 min. After heating at reflux for 2 h, the mixture was worked up as in the General Procedure. The resulting oil was chromatographed on silica gel using 1:9 ethyl acetate-60-80°C petroleum to remove traces of impurity; subsequent elution of the yellow band with 2:8 ethyl acetate-petroleum afforded a fraction which was evaporated to give 2 (1.55 g, 20%) as a yellow oil; IR 2975, 2940, 2860, 2820, 2770, 1705 (s), 1690 (s), 1575, 1085, 1035, 995, 935, 840 cm^{-1}; ^1H-NMR $(CD_3)_2CO$ delta 10.51 (1H, s), 10.48 (1H, s), 8.20 (1H, t, J= 0.7Hz), 3.63 (2H, d, J= 0.7Hz) 2.30 (6H, s) ^{13}C-NMR$(CD_3)_2CO$ delta 188.2(s), 187.8(s), 140.9(s), 138.1(s), 136.3(s), 133.2(d), 132.4(s), 131.2(s), 59.5(t), 45.3(q). MS: m/z 259.0173. M^+, Calc for $C_{11}H_{11}Cl_2NO_2$ = 259.0167; 261, 260, 259, 258, 217, 215, 123, 89, 58 (base peak), 42. When dialdehyde 2 was refluxed with hydroxylamine hydrochloride in 1:1 pyridine-ethanol, the dioxime hydrochloride separated as prisms, m.p. 252-253 °C (decomp.). Found: C, 40.56; H, 4.37; N, 12.57. Calc. for $C_{11}H_{14}Cl_3N_3O_2$: C, 40.45; H, 4.32; N, 12.87%.

Reaction of 2,4-Dichloro-3-(dimethylaminomethylene)-1,4-cyclohexadiene-1,5-dicarboxaldehyde 1a with Boron Trifluoride Etherate. A mixture of dialdehyde 1a[1] (0.20 g, 0.77 mmol) and $BF_3.Et_2O$ (0.05 ml) was stirrred in CH_2Cl_2 (5 ml) at 20 °C for 20 h. Water (2 ml) was then slowly added, and the mixture evaporated to a bulk of 5 ml. To this was added CH_2Cl_2 (10 ml) and water (3 ml). The mixture was shaken and the organic layer separated, washed with water (5 ml) and dried. Evaporation gave a residue which was recrystallised from ethyl acetate to give 3 (30 mg, 17 %) as needles, m.p. 102-104 °C (lit m.p.[9] 104-106°C; ^1H-NMR $(CDCl_3)$, delta 8.47 (1H, s), 10.43 (s, 3H). MS: m/z 229.9532. M^+, Calc. for $C_9H_4Cl_2O_3$ = 229.9538.

Preparation of Adduct 4. Dialdehyde 1c (0.572 g, 2.0 mmol) and hydroquinone (0.11 g, 1.0 mmol) were dissolved in a mixture of hot chloroform-ethyl acetate (1:1); petroleum (60-80 °C) was then added until a slight turbidity appeared. On standing at 25 °C the adduct 4 (0.58 g, 85%) crystallised as ruby-red needles, m.p. 155-158 °C; IR nu_{max} $CHBr_3$ 2970, 2870, 2850, 1650, 1580(s), 1270, 920, 870 cm^{-1}; ^1H-NMR $(CDCl_3$-$DMSOd_6)$ delta 2.00 (8H, m), 3.30 (4H, s), 3.72 (8H, m), 6.73 (4H, s), 7.82 (2H, s), 10.20 (4H, m). Found: C, 56.11; H, 4.70; N, 3.95. Calc. for $C_{32}H_{32}Cl_4N_2O_6$: C, 56.32; H, 4.73; N, 4.11%.

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