A New Chiral Electron Acceptor for Nonlinear Optical Materials

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New chiral electron acceptors based on the cyclobutenedione unit are proposed for production of new highly active nonlinear optical materials with perfectly aligned polarization in one dimension; the crystal structure of one such compound, DAD **3**, is reported.

To obtain nonlinear optical materials with highly efficient second harmonic generation (SHG), a high molecular hyperpolarizability (β) and a non-centrosymmetric crystal structure are required. For these objectives, new chiral electron acceptors based on the cyclobutenedione structure may be of use for nonlinear optical materials, centrosymmetric crystal structures being prevented by introduction of chirality and hydrogen bonding properties. Several new materials containing cyclobutenedione units have been synthesized. In particular, (−)-1-(4-dimethylaminophenyl)-2-(2-hydroxypropylamino)cyclobutene-3,4-dione (DAD) shows high SHG in powder method studies.[1] X-Ray analysis indicates that the direction of polarization of DAD in the molecular crystal is perfectly aligned in one dimension.

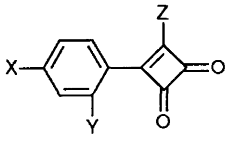
Owing to the large optical nonlinearity, the high threshold for laser damage, and the fast nonlinear response of organic crystals compared to inorganic counterparts, they are of particular interest. Organic molecules with one-dimensional delocalized π-conjugated systems, such as aromatic compounds and polydiacetylenes, are expected to demonstrate π-electron delocalization and intramolecular charge transfer. They have shown extremely large optical nonlinearities at the molecular level.[2] However, it is generally hard to control the molecular orientation in the desired way in the macroscopic crystalline state. At the macroscopic level, the overall nonlinear response of materials depends very critically on the relative orientation of molecules for second-order nonlinearity. Unfortunately, most organic molecules, particularly those with large ground state dipole moments, tend to form centrosymmetric structures.

To align molecular crystals in order to obtain polar structures, several methods have been used so far; hydrogen bonding properties,[3] chirality[4] *etc.* As the electron acceptor for nonlinear optical materials, almost all compounds include

Table 1 Spectroscopic properties and relative SHG intensities of cyclobutenediones **1–8** and the nitro analogue **9**

Material	X	Y	Z[a]	λ_{max}/nm[b]	ε[b]	SHG[c]
1	Me	H	OH	319	23 072	2.5
2	Me_2N	H	OH	379	23 850	0
3	Me_2N	H	$NHCH_2\mathit{C}H(OH)Me$	397	38 954	64
4	Me_2N	H	$NH\mathit{C}H(Et)CH_2OH$	396	39 051	6
5	Me_2N	H	$NH\mathit{C}H(CH_2Ph)CH_2OH$	394	35 325	8
6	Me_2N	H	$\overline{N(CH_2)_3\mathit{C}}HCO_2Bu^t$	396	28 780	8
7	Me_2N	Et	$NH\mathit{C}H(Et)CH_2OH$	397	18 373	26
8	$MeO(CH_2)_2(Me)N$	H	$NHCH_2\mathit{C}H(OH)Me$	397	47 842	58
9	*N,N*-Dimethylamino-*p*-nitroaniline			388	18 557	0

[a] Chiral centre is in italic type. [b] In EtOH solution. [c] Intensity relative to that of urea.



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nitro[5] or cyano groups. A new chiral cyclobutenedione-type electron acceptor for nonlinear optical materials is now proposed as an alternative conventional electron acceptors, centrosymmetric structures being prevented by introduction of chiral amino acid derivatives into the acceptor itself.

Such materials containing amino acid derivatives have now been synthesized (Table 1). They were identified by elemental analysis, mass spectrometry and IR spectroscopy. Full details of the syntheses will be reported elsewhere in the near future. Table 1 shows UV data and SHG intensities, determined by the powder method relative to urea (100–150 μm). SHG intensities were measured by detection with a photomultiplier of 532 nm light generated from the powder materials. Samples were held between two glass plates and set in an optical sphere. They were irradiated with a pulsed Nd:YAG laser at 1.064 μm (15 ns, 0.1 mJ/pulse). The X-ray crystal structure of compound **3** was determined.†

Table 1 shows that cyclobutenediones as electron acceptor for nonlinear optical materials have several advantages: the strong accepting property of the cyclobutenediones, their high molecular absorption coefficient, hydrogen bonding properties and easy introduction of various amino acid derivatives into their structure resulting in the formation of chiral nonlinear optical materials.

Although material **1** has a methyl substituent of lower donating ability bonded to the π-conjugated system, leading to λ_{max} at a shorter wavelength and a smaller dipole moment, material **1** shows fairly high SHG intensity, possibly owing to the hydrogen bonding capability of the hydroxycyclobutenedione unit. The absorption spectra of material **1** depend upon solvent: λ_{max} = 319 nm in EtOH, and 321 and 309 nm in CH_2Cl_2. The protic solvent EtOH forms a hydrogen bond with the material **1** and changes its electronic energy pattern.

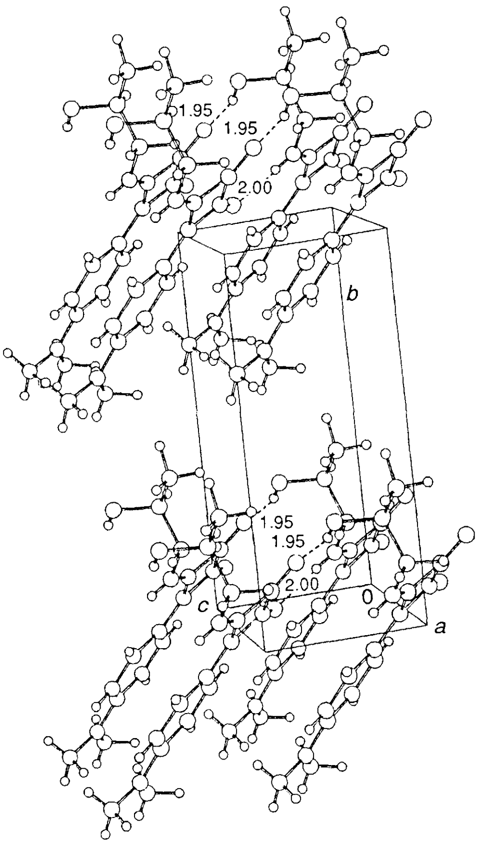

Fig. 1 Crystal structure of (−)-1-(4-dimethylaminophenyl)-2-(2-hydroxypropylamino)cyclobutene-3,4-dione (DAD), **3**

However, in the case of material **2**, the more highly donating amino group bonded to the π-conjugated system induces a larger ground state dipole moment than for material **1**. For material **2**, electrostatically favourable interactions with adjacent molecules are possible, which may result in the formation of a centrosymmetric crystal structure, despite the hydrogen bonding possibilities. Like *N,N*-dimethylamino-*p*-nitroaniline **9**, **2** did not generate SHG.

Even in molecules with large ground state dipole moments, which favour centrosymmetric structures, high SHG intensities were attained by introduction of asymmetric amino acid derivatives into the cyclobutenedione unit, leading to noncentrosymmetric crystal structures. Compounds **3–8** are examples of such materials, for which hydrogen bonding is possible and which also include chiral centres. These materials also show generally higher molecular absorption coefficients than the nitro analogue **9** suggesting that the oscillator strength and molecular hyperpolarizability of the cyclobutenedione units are enhanced.

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† X-Ray analysis was performed by Drs T. Hori and M. Furukawa, Rigaku Corporation. Cell parameters and intensity data were derived from measurements on four-circle diffractometer, Rigaku AFC5R, with graphite monochromated Cu-Kα radiation. Molecular and crystal structures were determined by the direct method by using the program of TEXSAN. Crystals were grown from methanol solution by slow evaporation. *Crystal data*: DAD, **3**, $C_{125}H_{18}N_2O_3$, space group $P1$ (No. 1), M = 274.32, a = 5.6932(6), b = 12.679(2), c = 5.250(1) Å, α = 93.79(2), β = 103.77(1), γ = 102.04(1)°, V = 357.3(1) Å^3, R = 0.041, R_w = 0.054, Z = 1, μ(Cu-Kα) = 6.96 cm^{-1}, 1038 reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

These advantages of the new chiral electron acceptor, as described above, are valuable in preventing centrosymmetric molecular structures, and lead to high SHG intensities. The molecular crystal of DAD **3**, in particular shows a high SHG in powder studies (64 times that of urea).

X-Ray crystallographic analysis of the DAD molecular crystal **3**† shows that it belongs to the triclinic system with the non-centrosymmetric space group $P1$ and that the direction of polarization of DAD is perfectly aligned in one dimension in spite of strong electrostatic repulsion, as shown in Fig. 1. It also indicates the existence of two hydrogen bonds between the two oxygen atoms of the cyclobutenedione and NH [1.95(6) Å] and OH groups [2.00(7) Å] of the amino alcohol of adjacent moelcules; the cyclobutenedione ring and the benzene ring of the dimethylanilino substituent are coplanar. The crystallographic results and UV spectrum of DAD **3** indicate that charge transfer in the DAD molecule mainly occurs from the dimethylanilino group to the cyclobutenedione ring to form a benzoquinoid structure, as seen in *p*-nitroaniline derivatives. As the particular tensor component of the DAD molecular crystal is expected to be very high, and greater than that of 2-methyl-4-nitroaniline (MNA),[6] it should become a most suitable material for a highly efficient frequency doubler optical device by use of phase matching with an optical waveguide. Its electrooptical properties may be interesting as well.

To summarize, cyclobutenediones are excellent electron acceptors for nonlinear optical materials, those including chiral amino acid units being particularly effective in controlling molecular alignment in the formation of molecular crystals.

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