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4-Dimethylamino-3-nitrocinnamic Acid, $C_{11}H_{12}N_2O_4$ (I), and 1-(4-Dimethylaminocinnamoyl)imidazole, $C_{14}H_{15}N_3O$ (II)*

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Abstract. (I) $M_r = 236\cdot2$, monoclinic, $P2_1/c$, $a = 18\cdot213\ (7)$, $b = 7\cdot111\ (5)$, $c = 8\cdot736\ (4)$ Å, $\beta = 93\cdot88\ (2)°$, $V = 1128\cdot8$ Å^3, $Z = 4$, $D_x = 1\cdot390$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 0\cdot92$ mm^{-1}, $F(000) = 496$, $T = 293$ K, final $R = 0\cdot047$, $wR = 0\cdot052$ on 1697 unique reflections. (II) $M_r = 241\cdot3$, monoclinic, $P2_1/c$, $a = 8\cdot375\ (7)$, $b = 6\cdot565\ (1)$, $c = 23\cdot783\ (9)$ Å, $\beta = 101\cdot81\ (4)°$, $V = 1280\cdot0$ Å^3, $Z = 4$, $D_x = 1\cdot252$ Mg m^{-3}, μ(Cu $K\alpha$) $= 0\cdot66$ mm^{-1}, $F(000) = 512$, $T = 293$ K, final $R = 0\cdot050$, $wR = 0\cdot054$ on 1861 unique reflections. By comparison with the structure of the substituted acid (I), there is a clear tendency in the imidazole derivative (II) toward quinonoid character and a significant lengthening and shortening of the ethylenic double and adjacent single bonds respectively. (I) is significantly non-planar because of overcrowding of substituents and even the benzene ring is slightly warped; (II) is more nearly planar.

Introduction. The protein papain forms enzyme-substrate intermediates with various cinnamic acid derivatives. The resonance Raman spectra of the intermediates are distinctly different from those of the unbound substrates (Carey, Carriere, Lynn & Schneider, 1976), and model compounds have been found that mimic the absorption and resonance Raman properties of the acyl enzymes and of the substrates. The spectral properties of 4-dimethylamino-3-nitrocinnamic acid (I) represent unbound substrate, while the spectra of 1-(4-dimethylaminocinnamoyl)imidazole (II) are similar to those of the acyl-enzyme intermediates (Carey, Carriere, Phelps & Schneider, 1978). X-ray analyses were undertaken to provide structural information to assist in the interpretation of the spectral data.

Experimental. (I) Dark yellow plates, $0\cdot80 \times 0\cdot40 \times 0\cdot10$ mm, (II) yellow prisms, $0\cdot35 \times 0\cdot50 \times 0\cdot55$ mm, Picker card-controlled diffractometer, Ni-filtered Cu radiation, $\theta/2\theta$ scans with 20 s background counts at beginning and end of each scan; scan ranges: (I) 2·0° for $2\theta \leq 60°$, 2·5° for $60 < 2\theta \leq 90°$ and 3·5° for $90 < 2\theta \leq 130°$; (II) 2·5° for $2\theta \leq 90°$ and 3·2° for $90 < 2\theta \leq 130°$; (I) all 1917 independent reflections with $2\theta \leq 130°$ measured, standard-reflection intensity fluctuations <1%, index range: h 0→21, k 0→8, l −10→10; 1697 reflections with net counts ≥8 (deca)counts and ≥10% of total background count considered observed, Lp and absorption corrections (max. and min. transmission coefficients 0·912 and 0·644), extinction correction ($g/\mu = 0\cdot8 \times 10^{-6}$) applied later, structure solved non-routinely with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), E maps corresponding to best two combined figures of merit obviously incorrect; correct solution derived from third map as the average of two images of the molecule. For (II) all 2170 independent reflections with $2\theta \leq 130°$ measured, standard-reflection intensity fluctuation ≤2·0%, index range: h −9→9, k 0→7, l 0→27; 1861 reflections with net counts ≥15 (deca)counts and ≥10% of total background count considered observed, Lp corrections applied, absorption ignored, extinction correction ($g/\mu = 0\cdot32 \times 10^{-6}$) applied during refinement, structure solved by symbolic addition method. Both (I) and (II) refined by block-diagonal least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, non-hydrogen atoms refined first isotropically, subsequently anisotropically, H atoms located on difference maps and refined isotropically, scattering factors taken from *International Tables for X-ray Crystallography* (1974); both weighting schemes of the form $\sqrt{w} = w_1 \times w_2$, where $w_1 = 25\cdot0/|F_o|$ if $|F_o| > 25\cdot0$, $w_1 = 1\cdot0$ otherwise, and $w_2 = \sin^2\theta/P_2$ if $\sin^2\theta < P_2$, $w_2 = 1\cdot0$ otherwise, with $P_2 = 0\cdot5$ for (I) and $0\cdot3$ for (II). These weighting schemes made $\langle w\Delta^2\rangle$ essentially independent of $|F_o|$ and $\sin^2\theta$. Two reflections (I) and four reflections (II) showing poor agreement were given zero weights during final refinement cycles. In (I), hydrogen atom of carboxylic acid group found to be disordered. Initial refinement with 50% occupancy assigned at each of two sites led to an unexpectedly large temperature factor at the site closest to O(11). When permitted to vary, the occupancy factors took on values close to 0·60 [near O(10)] and 0·40 [near O(11)] and simultaaneously the temperature factors became more nearly equal. Although the difference in the occupancy factors was not statistically significant, the values were accep-

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ted. In last least-squares cycle $(\Delta/\sigma)_{\rm max} = 0{\cdot}24$ (I), 0·33 (II) and $(\Delta/\sigma)_{\rm mean} = 0{\cdot}05$ (I), 0·08 (II). For (I), final $R = 0{\cdot}047$, $wR = 0{\cdot}052$, $\Delta\rho_{\rm max} = 0{\cdot}19$, $\Delta\rho_{\rm min} = -0{\cdot}21$, and for (II), $R = 0{\cdot}050$, $wR = 0{\cdot}054$, $\Delta\rho_{\rm max} = 0{\cdot}12$, $\Delta\rho_{\rm min} = -0{\cdot}19$ e Å^{-3}. R and wR values for both structures are for all observed reflections. Computer programs of Ahmed, Hall, Pippy & Huber (1973) and of Johnson (1971) used.

Discussion. Atomic parameters for the two compounds are listed in Tables 1 and 2.* Bond lengths and the numbering systems are shown in Fig. 1, and the bond angles are given in Fig. 2. The lengths of the C—H bonds for both structures vary between 0·90 and 1·02 Å. **TLS** analyses (Schomaker & Trueblood, 1968) showed that neither of the two molecules could be described satisfactorily as a rigid body, although in each case the principal libration was about the long axis of the molecule with an amplitude of over 4·5°.

The bond lengths and angles in the substituted acid are quite similar to those found in other cinnamic acid structures (Bryan & Forcier, 1980; Bryan & Freyberg, 1975; Bryan & Hartley, 1981; Glusker, Zacharias & Carrell, 1975). However, important differences in bond lengths (0·013 to 0·016 Å, $>3{\cdot}5\sigma$) are observed between (I) and (II) in the bond sequence C(3)—C(2), C(2)—C(1), C(1)—C(7), C(7)—C(8), C(8)—C(9). Bonds C(3)—C(2), C(1)—C(7) and C(8)—C(9) are shorter in the imidazole compound (II) while C(2)—C(1) and C(7)—C(8) are longer, suggesting considerable quinonoid character in the ring and double-bond delocalization in the side chain for the amide. Such polarization is not unexpected, given the strong electron donor (dimethylamino group) at one end of the molecule and the electron-attracting imidazole group at the other. It seems possible that a similar highly polarized π-electron system may occur in the substrate at the active site by interaction of the acyl residue with protein dipoles and/or hydrogen bonds.

Interestingly, there are some significant differences between bond lengths in the side chain of (I) and corresponding values in the methyl ester of 4-hydroxy-3-nitrocinnamic acid (Hanson, 1975). The double bond in the ester is shorter [1·308 (4) Å] and the adjacent single bonds are longer [1·468 (3) and 1·471 (3) Å] than in (I). Thus, while the electron system in (II) is more delocalized than in (I), the ester seems to show even less delocalization than (I). In the aromatic-ring moiety, the longer C(2)—C(3) bond compared to C(5)—C(6) in (I) is echoed in the ester, where the difference is also 0·019 Å.

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic temperature factors for* 4-*dimethylamino*-3-*nitrocinnamic acid*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
C(1)	2931 (1)	211 (3)	4597 (2)	3·5
C(2)	2179 (1)	528 (2)	4412 (2)	3·3
C(3)	1744 (1)	499 (2)	5650 (2)	3·1
C(4)	2022 (1)	35 (2)	7156 (2)	3·1
C(5)	2796 (1)	−202 (3)	7315 (2)	3·9
C(6)	3226 (1)	−120 (3)	6096 (2)	4·0
C(7)	3373 (1)	244 (3)	3269 (2)	4·0
C(8)	4086 (1)	−104 (4)	3240 (2)	4·9
C(9)	4470 (1)	−52 (4)	1827 (2)	4·8
O(10)	4112 (1)	273 (4)	574 (2)	6·5
O(11)	5150 (1)	−333 (5)	1920 (2)	7·4
N(12)	997 (1)	1202 (2)	5322 (2)	3·6
O(13)	656 (1)	673 (3)	4155 (2)	5·2
O(14)	765 (1)	2371 (2)	6202 (2)	5·1
N(15)	1601 (1)	−219 (2)	8365 (2)	3·6
C(16)	835 (1)	−802 (3)	8193 (2)	4·5
C(17)	1955 (1)	−433 (3)	9898 (2)	4·2

Table 2. *Fractional atomic coordinates* (×10^4 *for x and y*, ×10^5 *for z*) *and equivalent isotropic temperature factors for* 1-(4-*dimethylaminocinnamoyl*)*imidazole*

	x	y	z	$B_{\rm eq}$(Å^2)*
C(1)	1491 (3)	5889 (3)	9397 (8)	4·2
C(2)	1987 (3)	5099 (3)	14952 (8)	4·5
C(3)	2877 (3)	3348 (3)	15986 (8)	4·8
C(4)	3355 (3)	2245 (3)	11523 (9)	4·4
C(5)	2872 (3)	3046 (4)	5936 (9)	4·9
C(6)	1986 (3)	4807 (3)	4976 (8)	4·9
C(7)	538 (3)	7719 (3)	8102 (8)	4·4
C(8)	−17 (3)	8938 (3)	11803 (8)	4·3
C(9)	−979 (3)	10715 (3)	9785 (8)	4·2
O(10)	−1476 (2)	11188 (3)	4806 (6)	5·6
N(11)	4213 (2)	481 (3)	12544 (8)	5·3
C(12)	4702 (3)	−637 (4)	7937 (12)	6·1
C(13)	4715 (4)	−302 (4)	18334 (12)	6·7
N(14)	−1410 (2)	12005 (2)	14071 (6)	3·9
C(15)	−946 (3)	11886 (3)	19942 (8)	4·8
N(16)	−1523 (3)	13376 (3)	22486 (8)	5·6
C(17)	−2407 (4)	14535 (4)	18092 (11)	6·0
C(18)	−2343 (3)	13736 (4)	12978 (9)	5·4

* As defined in Table 1.

4-Dimethylamino-3-nitrocinnamic acid is significantly nonplanar with deviations up to 1·02 Å [O(14)] from the mean molecular plane. The nitro group is bent and twisted 45·3 (2)° out of the mean plane of the benzene ring and the dimethylamino group is also twisted 20·3 (2)° out of the same plane. The benzene ring is itself warped because of the overcrowding caused by adjacent nitro and dimethylamino groups; C(3) and C(4) are displaced −0·029 (2) and 0·032 (2) Å respectively from the mean plane. The acid side chain is planar within 0·019 (2) Å.

The amide (II) is much more nearly planar. The largest deviation is 0·126 (2) Å [N(16)] from a mean plane through all non-hydrogen atoms. The imidazole ring is planar and makes an angle of 8·47 (3)° with the mean plane through the remaining non-hydrogen atoms.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42118 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

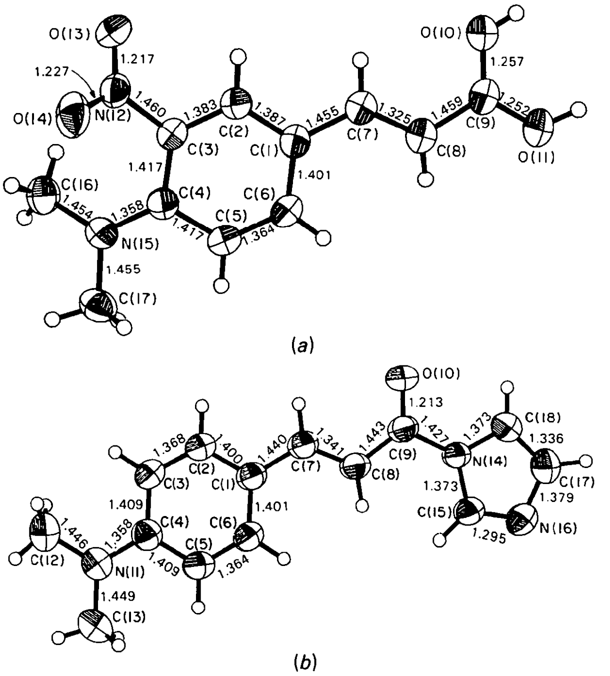

Fig. 1. *ORTEP* views of the two molecules showing the numbering schemes used and the bond lengths (Å). The ellipsoids (for the non-hydrogen atoms) contain 50% probability; hydrogens are shown as spheres of 0·1 Å radius. E.s.d.'s of the bond lengths are 0·002–0·003 Å. (*a*) 4-Dimethylamino-3-nitrocinnamic acid. (*b*) 1-(4-Dimethylaminocinnamoyl)imidazole.

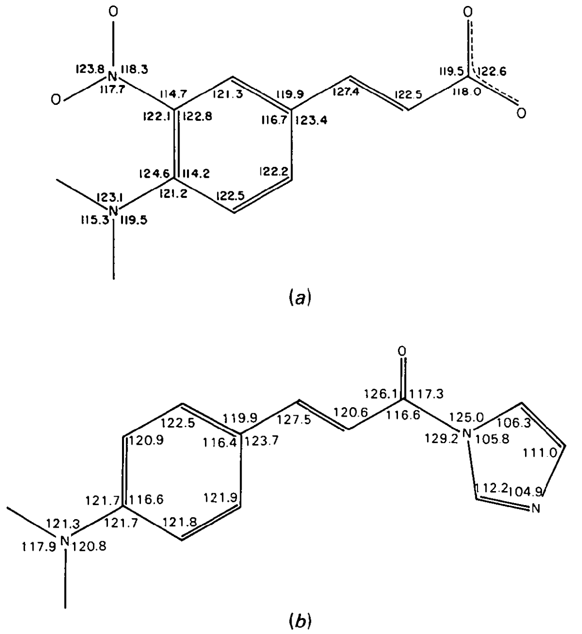

Fig. 2. Bond angles (°). E.s.d.'s are 0·14–0·23°. (*a*) 4-Dimethylamino-3-nitrocinnamic acid. (*b*) 1-(4-Dimethylaminocinnamoyl)imidazole.

As observed in various other cinnamic acid structures (Bryan & Hartley, 1981; Bryan & Freyberg, 1975; Glusker *et al.*, 1975; Filippakis, Leiserowitz, Rabinovich & Schmidt, 1972) the molecules of (I) form hydrogen-bonded dimers, in which the carboxyl groups are disordered. The lengths of the C—O bonds are not significantly different (see Fig. 1), and the partial occupancy of two sites by the carboxyl hydrogen atom is consistent with this. The packing arrangements are shown in Fig. 3. The intermolecular contact C(15)—H(151)···N(16) in (II) is short, 2·40 (2) Å, and very probably represents a hydrogen bond. Because C(15) is adjacent to two nitrogen atoms, the C—H atoms can be considered as particularly likely to participate in such a bond (Taylor & Kennard, 1982). There are no other intermolecular distances shorter than van der Waals contact distances.

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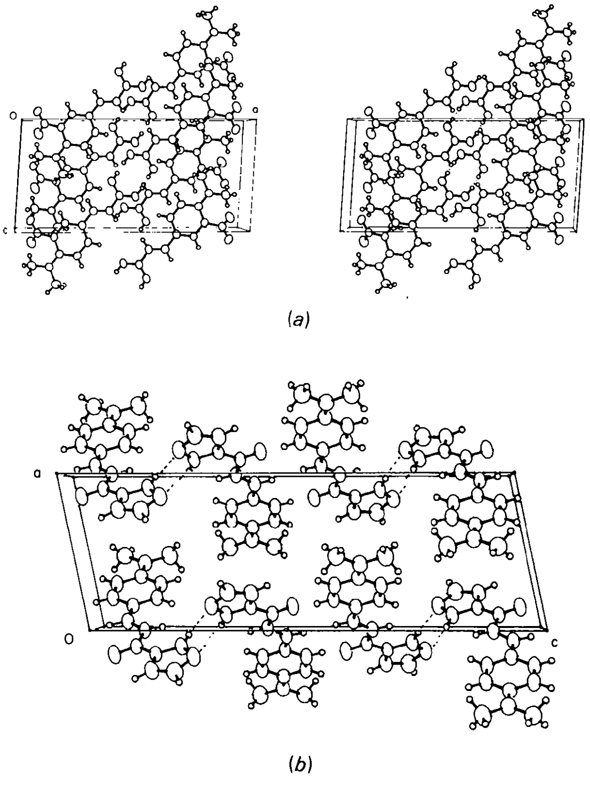

Fig. 3. Packing arrangements. Hydrogen bonds are indicated by dashed lines. (*a*) Stereoview of 4-dimethylamino-3-nitrocinnamic acid. *a* horizontal, *c* vertical. (*b*) Perspective view of 1-(4-dimethylaminocinnamoyl)imidazole. *a* vertical, *c* horizontal.

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2,3,3a,4,5,8-Hexachloro-3a,6,7,7a-tetrahydro-1,6-methano-1*H*-indene (γ-Chlordene), $C_{10}H_6Cl_6$

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Abstract. $M_r = 338\cdot8$, monoclinic, $P2_1/n$, $a = 8\cdot936\ (1)$, $b = 14\cdot372\ (3)$, $c = 9\cdot774\ (2)$ Å, $\beta = 100\cdot72\ (1)°$, $V = 1233\cdot4\ (5)$ Å^3, $Z = 4$, $D_x = 1\cdot82$ Mg m^{-3}, Mo $K\alpha_1$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot35$ mm^{-1}, $F(000) = 672$, $T = 293$ K, $R = 0\cdot039$ for 1326 unique observed reflections. The compound used was supplied as an Environmental Protection Agency (US) analytical standard. The structure is similar to the product formed by ozonolysis of γ-chlordene, except for the differences due to the effect of removal of one of the ethylene links. It is a bridged chlorinated cyclodiene but without the basic hexachloronorbornene nucleus common to cyclodiene insecticides.

Introduction. The title compound (1) is one of three bridged structural isomers designated α, β, γ of formula $C_{10}H_6Cl_6$ isolated from technical chlordane insecticide (Sovocool, Lewis, Harless, Wilson & Zehr, 1977). The crystal structure of the α-isomer has been determined (Smith, Kennard & Palm, 1981). There is 9% of the γ-isomer in the technical insecticide (Parlar, Hustert, Gäb & Korte, 1979). It is less toxic to *Musca domestica* than the α-isomer but more toxic to *Spodoptera littoralis* (Gäb, Cochrane, Parlar & Korte, 1975). The structure was determined to verify the assignment based on ^{1}H NMR and gas chromatography–mass spectroscopy evidence (Cochrane, Parlar, Gäb & Korte, 1975; Wilson & Sovocool, 1977).

Experimental. Colourless crystals, m.p. 400–401 K, obtained from isopropyl alcohol. 1955 reflections ($2\theta_{\max} = 50°$, h 0–±6, k 0–16, l 0–11) collected from one crystal, size $0\cdot28 \times 0\cdot21 \times 0\cdot13$ mm, mounted on CAD-4 diffractometer. 22 non-axial high-angle ($28 < 2\theta < 30°$) reflections used for lattice-parameter determination. Systematic absences $h0l$ ($h + l = 2n + 1$), $0k0$ ($k = 2n + 1$) indicated non-standard space group $P2_1/n$ (standard $P2_1/c$). No absorption correction. Standard reflections 246 [2260 (75)], 382 [1714 (90)], $3\bar{8}2$ [1826 (80)]; reflections measured = 1955, unique = 1726, significant = 1326 [$I > 2\cdot5\sigma(I)$]; time of exposure 39 h. Structure solution by multisolution $\sum_2$ sign expansion direct methods of *SHELX*76 (Sheldrick, 1976). Least-squares refinement (F's) with anisotropic thermal parameters on all non-hydrogens gave $R = 0\cdot039$, $wR = 0\cdot044$. Hydrogens located from

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