Ottersen, T. (1977). *Acta Chem. Scand. Ser. A*, **31**, 480–484.
Pèpe, G. & Siri, D. (1990). *Studies in Physical and Theoretical Chemistry*, Vol. 71, pp. 93–101.
Rahal, H. (1991). Thesis, Univ. Aix-Marseille II, France.
Reboul, J. P., Pèpe, G., Siri, D., Oddon, Y., Rahal, H., Soyfer, J. C. & Barbe, J. (1992). *Acta Cryst.* C**48**, 111–115.
Reboul, J. P., Rahal, H., Pèpe, G., Oddon, Y., Siri, D., Astier, J. P., Soyfer, J. C. & Barbe, J. (1992). *Acta Cryst.* C**48**, 2157–2160.
Romming, C., Seip, H. M. & Aanesen Oymo, I.-M. (1974). *Acta Chem. Scand. Ser. A*, **28**, 507–514.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Shukla, A. P., Galy, A. M., Brouant, P., Galy, J. P., Soyfer, J. C. & Barbe, J. (1985). *VIIth Int. Symp. Med. Chem. Proced.*, Vol. 2, pp. 213–214. Stockholm: Swedish Pharmaceutical Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Structure of MAP:MNA, the 1:1 Adduct Between (*R*)-Methyl 2-(2,4-Dinitroanilino)propanoate (MAP) and 2-Methyl-4-nitroaniline (MNA), a New Nonlinear Optical Crystal

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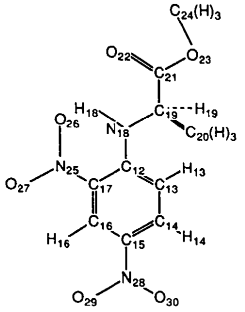
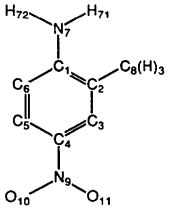
Abstract. MAP:MNA, (*R*)-methyl 2-(2,4-dinitroanilino)propionate–2-methyl-4-nitroaniline (1/1), $C_{10}H_{11}N_3O_6.C_7H_8N_2O_2$ ($=C_{17}H_{19}N_5O_8$), $M_r = 421.37$, monoclinic, $P2_1$, $a = 6.9196$ (5), $b = 7.673$ (8), $c = 18.554$ (1) Å, $\beta = 92.547$ (6)°, $V = 984.1$ Å^3, $Z = 2$, $D_x = 1.422$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.075$ cm^{-1}, $F(000) = 440$, $T = 295$ (3) K, $R = 0.0445$, $wR = 0.0440$, for 1783 observed reflections. The molecules are stacked MAP atop MNA, inclined to the approximate stack axis [010] by 23.44 (MAP) and 26.73° (MNA); an intermolecular hydrogen bond (2.367 Å) occurs in the [101] direction between a nitro O atom of MAP and an amino H atom of MNA. The INDO molecular dipole moments of MAP and MNA form a mutual angle of 127.2°. A powder sample shows significant frequency-doubling intensity.

Introduction. We report here the crystal and molecular structure of the 1:1 adduct MAP:MNA, which was obtained from two known organic molecules, MAP [(*R*)-methyl 2-(2,4-dinitroanilino)propanoate, also known as (*R*)-*N*-(2,4-dinitrophenyl)methyl alaninate] and MNA (2-methyl-4-nitroaniline, also known as *p*-nitro-*o*-toluidine).



MAP



MNA

Crystal structures have been determined previously for the separate components: MAP (Knossow, Mauguen & de Rango, 1976) and MNA (Levine, Bethea, Thurmond, Lynch & Bernstein, 1979; Lipscomb, Garito & Narang, 1981). The optical nonlinearities of both MAP and MNA have been studied (Oudar & Hierle, 1977; Levine, Bethea, Thurmond, Lynch & Bernstein, 1979; Oudar & Zyss,

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1982). Table 1 gives crystallographic parameters for MAP, MNA and MAP:MNA. The crystal growth techniques and the Raman spectra of MAP:MNA are reported elsewhere (Rao, Batra, Lal, Evens, Loo, Metzger & Lee, 1991).

Individual organic molecules often have a significant nonlinearity at optical frequencies, *i.e.* they exhibit a field-dependent and frequency-dependent molecular moment $\mu(E,\nu)$ which, in addition to a field-independent electric dipole moment μ_0, has appreciable higher moments induced by the electric field $\mathbf{E}(\nu)$ owing to the photons of frequency ν and energy $h\nu$: one uses the Maclaurin expansion in $\mathbf{E} = \mathbf{E}(\nu)$:

$$\begin{aligned}\mu_i(E) = \mu_{0i} &+ \textstyle\sum_k \alpha_{ik} E_k + \sum_j \sum_k \beta_{jk} E_j E_k \\ &+ \textstyle\sum_j \sum_k \sum_l \gamma_{ijkl} E_j E_k E_l \\ &+ \textstyle\sum_j \sum_k \sum_l \sum_m \delta_{ijklm} E_j E_k E_l E_m + \cdots\end{aligned}$$

where α (β, γ, δ,...) are the molecular frequency-dependent polarizability (hyperpolarizability) tensors of rank two (three, four,...). In the bulk the corresponding macroscopic polarization $\mathbf{P} = \mathbf{P}(\mathbf{E},\nu)$ is often abbreviated as the tensor sum:

$$\begin{aligned}\mathbf{P}(\mathbf{E},\nu) = \mathbf{P}_0 + \chi^{(1)}\mathbf{E} + \chi^{(2)}\text{: } \mathbf{EE} + \chi^{(3)}\text{: } \mathbf{EEE} \\ + \chi^{(4)}\text{: } \mathbf{EEEE} + \ldots\end{aligned}$$

where the $\chi^{(n)}$ are the nth-order nonlinear electrical (optical) susceptibilities. The crystalline even-order susceptibilities $\chi^{(2)}$, $\chi^{(4)}$ are non-zero if and only if the crystal belongs to a non-centrosymmetric space group. All this is of some interest, because, while infrared lasers (*e.g.* GaAs|GaAlAs) are cheap and plentiful, there are no practical light-weight lasers that operate in the 200 to 500 nm (UV to visible) region of the electromagnetic spectrum. Materials with high $\chi^{(2)}$ (*e.g.* $LiNbO_3$) can frequency-double an IR beam into the visible range, provided that one can also meet the two ancillary requirements of large single crystals with smooth faces, and of efficient coupling of light energy into and out of the crystal (phase matching). Organic crystals have much higher $\chi^{(2)}$ values than inorganic crystals, but, at present, the size and quality of crystals remain unsatisfactory (Prasad & Williams, 1991).

Table 1. *Crystallographic parameters for three relevant non-centrosymmetric organic crystals*

Crystal	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ (°)	Space group	Class
MAP*	6.829	8.116	11.121	90	90	95.59	$P2_1$ (No. 4)	2
MNA†	8.225	11.620	7.585	90	94.08	90	*Ia* (No. 9)	*m*
MAP:MNA‡	6.920	7.673	18.554	90	92.6	90	$P2_1$ (No. 4)	2

*Knossow, Mauguen & de Rango (1976).
†Lipscomb, Garito & Narang (1981).
‡This study.

Table 2. *Atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

For H atoms, U are listed, as used in the formula $\exp(-0.25U\sin^2\theta/\lambda^2)$; for non-H the non-orthogonal tensor components U_{ij} are used in the formula $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + \ldots + 2a^*b^*U_{12}hk + \ldots)]$, and the entries below are U_{eq} = 1/3(the trace of the orthogonalized U tensor).

	x	y	z	U or U_{eq}
C1	−0.2719 (5)	0.1384	0.1594 (2)	0.056
C2	−0.0957 (5)	0.2123 (6)	0.1379 (2)	0.058
C3	0.0440 (5)	0.2515 (7)	0.1907 (2)	0.054
C4	0.0136 (4)	0.2192 (6)	0.2624 (1)	0.050
C5	−0.1586 (4)	0.1486 (6)	0.2833 (2)	0.053
C6	−0.2994 (5)	0.1090 (6)	0.2323 (2)	0.059
N7	−0.4168 (6)	0.0955 (7)	0.1101 (2)	0.082
C8	−0.0622 (8)	0.2461 (8)	0.0596 (2)	0.085
N9	0.1618 (4)	0.2629 (5)	0.3164 (1)	0.060
O10	0.1280 (4)	0.2411 (6)	0.3801 (1)	0.089
O11	0.3153 (4)	0.3197 (7)	0.2981 (1)	0.095
C12	−0.0316 (4)	0.6978 (5)	0.2680 (1)	0.044
C13	−0.2092 (4)	0.6155 (6)	0.2820 (2)	0.051
C14	−0.3455 (5)	0.5808 (6)	0.2296 (2)	0.054
C15	−0.3131 (4)	0.6272 (6)	0.1589 (2)	0.052
C16	−0.1464 (4)	0.7068 (6)	0.1411 (2)	0.051
C17	−0.0052 (4)	0.7427 (6)	0.1942 (1)	0.044
N18	0.1023 (3)	0.7302 (6)	0.3209 (1)	0.051
C19	0.0879 (4)	0.6884 (6)	0.3963 (2)	0.050
C20	−0.0425 (5)	0.8161 (8)	0.4354 (2)	0.065
C21	0.2919 (4)	0.6954 (6)	0.4295 (2)	0.055
O22	0.4302 (3)	0.7421 (6)	0.3986 (1)	0.080
O23	0.2963 (3)	0.6492 (6)	0.4977 (1)	0.080
C24	0.4805 (8)	0.665 (1)	0.5384 (3)	0.104
N25	0.1649 (3)	0.8304 (5)	0.1718 (1)	0.053
O26	0.2979 (3)	0.8611 (6)	0.2166 (1)	0.068
O27	0.1752 (3)	0.8742 (6)	0.1085 (1)	0.072
N28	−0.4594 (4)	0.5892 (6)	0.1017 (2)	0.068
O29	−0.4255 (4)	0.6290 (8)	0.0405 (1)	0.110
O30	−0.6106 (4)	0.5206 (6)	0.1186 (2)	0.087
H3	0.159 (4)	0.295 (4)	0.179 (2)	0.052 (9)
H5	−0.167 (4)	0.140 (5)	0.331 (2)	0.058 (9)
H6	−0.420 (5)	0.068 (4)	0.244 (2)	0.051 (8)
H71	−0.374 (5)	0.113 (6)	0.066 (2)	0.08 (1)
H72	−0.549 (9)	0.05 (1)	0.127 (3)	0.16 (3)
H81	−0.165 (7)	0.325 (9)	0.041 (3)	0.13 (2)
H82	−0.044 (7)	0.13 (1)	0.030 (3)	0.14 (2)
H83	0.072 (5)	0.271 (6)	0.051 (2)	0.08 (1)
H13	−0.234 (4)	0.584 (4)	0.329 (2)	0.043 (7)
H14	−0.466 (5)	0.538 (5)	0.241 (2)	0.07 (1)
H16	−0.122 (4)	0.736 (5)	0.098 (2)	0.060 (9)
H18	0.216 (5)	0.776 (5)	0.306 (2)	0.063 (9)
H19	0.039 (5)	0.576 (6)	0.403 (2)	0.08 (1)
H201	−0.178 (5)	0.808 (5)	0.418 (2)	0.065 (9)
H202	−0.043 (5)	0.787 (6)	0.486 (2)	0.08 (1)
H203	0.016 (6)	0.929 (6)	0.434 (2)	0.09 (1)
H241	0.460 (5)	0.624 (6)	0.582 (2)	0.08 (1)
H242	0.523 (8)	0.78 (1)	0.535 (3)	0.13 (2)
H243	0.575 (7)	0.599 (9)	0.512 (3)	0.12 (2)

Experimental. The synthesis, crystal growth, cleavage plane, and visible and Raman spectra of MAP: MNA have been reported elsewhere (Rao, Batra, Lal, Evans, Loo, Metzger & Lee, 1991).

From a batch of orange plate-like crystals, a small specimen (0.2 × 0.8 × 1.1 mm) was mounted on an Enraf–Nonius CAD-4F automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The unit cell and the orientation matrix were found by a least-squares fit to 24 reflections in the range $\theta = 9$–18°. The space group ($P2_1$) was determined by the systematic absence $00l$, l = odd. A data set (quadrant) was collected in the ω–2θ scan mode, with Bragg angle range θ = 1–25° and index range h = 0 to 8, k = 0 to 9, l = −22 to 22, and with scan-width parameters $\Delta\omega_a = 0.8$, $\Delta\omega_b = 0.20$°. The intensity control reflections were 200, 040 and 006; their intensity fluctuated less than 1% during data collection. Of 1999 unique data measured, 313 were labeled 'weak' during the pre-scan sequence of the data collection, but 1783 were observed to have measurable intensity, and were included in the data analysis. The data were corrected for Lorentz and polarization factors, but no correction for absorption was made. From visual inspection of a larger crystal mounted and aligned on the diffractometer, the predominant crystal face, and cleavage plane, was determined to be (001) (Rao, Batra, Lal, Evans, Loo, Metzger & Lee, 1991).

The structure was solved by direct methods. The H atoms were found on difference Fourier maps. The structure was refined by full-matrix weighted least squares, using anisotropic thermal parameters for all non-H atoms and isotropic thermal parameters for the H atoms, to a final weighted R index of 4.40% (unweighted R index 4.45%; 1783 observations, 346 parameters). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with weights given by $w = [\sigma(F_{hkl})^2 + 0.005F_{hkl}{}^2]^{-1}$. The final maximum shift/e.s.d. was 0.214. The largest peak in the final difference Fourier map was close to the O27-atom position, with a density of 0.167 e Å^{-3}.

The programs used were *DATRDN* (Hunter, 1982), *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976), *ORTEP*II (Johnson, 1976), *CELMAP* (Metzger, 1976) for least-squares planes, *CNINDO* (Pople & Beveridge, 1969; Dobosh, 1967) for INDO (intermediate neglect of differential orbitals) charges and dipole moments, and *EWALD* (Metzger, 1976, 1981) for lattice energies. The atomic scattering factors used were those of *SHELX*76.

Discussion. The atom positions are given in Table 2. A stereoscopic illustration of the packing in the unit cell is given in Fig. 1.*

The structure consists of sheets of MAP and MNA molecules that lie approximately in the (101) plane, and that stack approximately along [010]. The benezene rings of MAP and MNA are almost parallel to each other (the dihedral angle is only 4.41°), but are tilted with respect to the stack axis [010] by 23.44 (MNA) and 26.73° (MAP). The molecules are so stacked that the benzene C atoms are almost eclipsed; the amine group of MNA is below a nitro group of MAP (N7 almost eclipses N28); while the nitro group on MNA is below the aminopropanoate group N atoms of MAP (N9 almost eclipses N18). The average of the ten intermolecular MAP···MNA non-bonded distances (< 3.7 Å) is 3.556 Å.

There is an intermolecular hydrogen bond between the H71 atom of MNA and O29 of MAP (O29···H71 = 2.367 Å approximately along [101]), while there is no hydrogen bond to O30 (H71···O30 = 3.493 Å). Other parameters of the hydrogen bond are: the non-bonded distance N7···O29 = 2.965 Å; the bonded distance N7–H71 = 0.90 Å; two significant angles N7—H71···O29 = 102.5, N29—O29···H71 = 69.9°; the distance of H71 from the plane defined by the nitro-group atoms N28, O29, O30 is 0.131 Å.

The calculated INDO molecular dipole moments are 8.328 debyes (1 D $\simeq 3.33564 \times 10^{-30}$ C m) for the MAP part (oriented close to the vector from atom C16 to the midpoint between the C12 and the C13 atoms), and 6.995 D (oriented close to the C4···C1 vector) for the MNA part. The dipole moments form angles of 97.6 (MAP) and 102.6° (MNA) with the [010] axis and a mutual angle of 127.2°. The intermolecular Madelung (charge–charge) energy, based on the point charges,* is −35.215 kJ mol.$^{-1}$

The crystal structure shows alternating perpendicular π overlap between the almost eclipsed stacked aromatic rings of the MAP and MNA moieties, stacked at typical van der Waals distances. Since MAP is chiral (at atom C19), the structure is non-centrosymmetric. Although there is perpendicular stacking of the amine group of MNA over one nitro group of MAP, the computed INDO molecular dipole moments do not cancel. The opinion that polar molecules prefer centrosymmetric crystal structures is not supported by statistical comparison of 368 known centrosymmetric and non-centrosymmetric structures and computed AM1 molecular dipole moments (Whitesell, Davis, Saunders, Wilson & Feagins, 1991). The infinite network motif of hydrogen bonds in MNA and in several other nitroanilines (Panunto, Urbanczyk-Lipkowska, Johnson & Etter, 1987) is absent in MAP; in MAP:MNA it is replaced by a localized hydrogen bond between H71 of MNA and one O atom of a nitro group of MAP. The packing seems to be dominated by π–π interactions between the MAP and MNA molecules (which may explain the color of the crystals, which may be a result of a weak charge-transfer interaction between MAP and MNA), with some contribution from the localized hydrogen bond.

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* Lists of anisotropic thermal parameters, bond distances and angles, relevant bond lengths in the MAP:MNA structure compared with the previously determined MAP and MNA structures, equations for the least-squares planes, semiempirical INDO net atomic charges z_i and the atom-in-molecule molecular dipole moments resulting from *sp* hybridization $\mu_i^{\rm hyb}$, and observed and calculated structure-factor amplitudes, as well as a plot of the hydrogen bonding between one MNA and one MAP molecule in the (101) plane, and two plots of the overlap between MAP and MNA along the stack axis [010], projected onto MAP and seen from the side, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55399 (50 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0068]

* See deposition footnote.

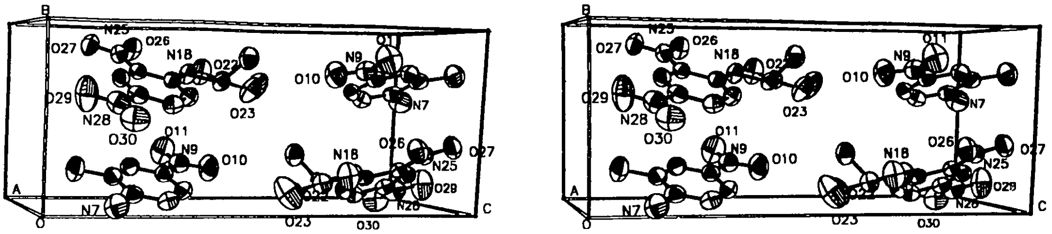

Fig. 1. Stereoscopic *ORTEP*II drawing (Johnson, 1976) of the molecular packing within the unit cell, projected onto the (011) plane. H atoms are omitted.

It is hoped that the crystal will be a good frequency doubler, with good coupling of light in and out of the (001) face. The molecular dipoles are slanted somewhat away from the (001) face normal, so maybe the electric vector of incoming laser radiation will form a significant dot product with the largest expected $\chi^{(2)}_{ijk}$ component (which should be approximately parallel to the resultant of the molecular dipoles). It is significant that the powder second-harmonic generation efficiency (intensity of green light produced at 532 nm from irradiation at 1064 nm from a pulsed Nd:YAG laser) was found in a preliminary experiment to be the same as that of MAP, but less than that of MNA (Rao, Batra, Lal, Evans, Loo, Metzger & Lee, 1991).

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References

Dobosh, P. A. (1967). *Quantum Chem. Program Exch.* **11**, 141.
Hunter, W. E. (1982). *DATRDN*. Univ. of Alabama, USA.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Knossow, M., Mauguen, Y. & de Rango, C. (1976). *Cryst. Struct. Commun.* **5**, 719–722.
Levine, B. F., Bethea, L. G., Thurmond, C. D., Lynch, R. T. & Bernstein, J. L. (1979). *J. Appl. Phys.* **50**, 2523–2527.
Lipscomb, G. F., Garito, A. F. & Narang, R. S. (1981). *J. Chem. Phys.* **75**, 1509–1516.
Metzger, R. M. (1976). *J. Chem. Phys.* **64**, 2069–2075.
Metzger, R. M. (1981). Editor. *Cohesive Energy and Ionicity, Springer Topics in Current Physics*, Vol. 26. New York: Springer.
Oudar, J. L. & Hierle, R. (1977). *J. Appl. Phys.* **48**, 2699–2704.
Oudar, J. L. & Zyss, J. (1982). *Phys. Rev. A*, **26**, 2016–2027.
Panunto, T. W., Urbanczyk-Lipkowska, Z., Johnson, R. & Etter, M. C. (1987). *J. Am. Chem. Soc.* **109**, 7786–7797.
Pople, J. A. & Beveridge, D. L. (1969). *Approximate Molecular Orbital Theory*. New York: McGraw-Hill.
Prasad, P. N. & Williams, D. J. (1991). *Introduction to Nonlinear Optical Effects in Molecules and Polymers*. New York: Wiley.
Rao, S. M., Batra, A. K., Lal, R. B., Evans, R. A., Loo, B. H., Metzger, R. M. & Lee, W. J. (1991). *J. Appl. Phys.* **70**, 6674–6678.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
Whitesell, J. K., Davis, R. E., Saunders, L. L., Wilson, R. J. & Feagins, J. P. (1991). *J. Am. Chem. Soc.* **113**, 3267–3270.

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Structure and Crystal Packing of the Antibacterial Drug 1-{[(5-Nitro-2-furanyl)methylene]amino}-2,4-imidazolidinedione (Nitrofurantoin)

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Abstract. $C_8H_6N_4O_5$, $M_r = 238.16$, monoclinic, $P2_1/n$, $a = 7.845$ (1), $b = 6.462$ (3), $c = 18.920$ (4) Å, $\beta = 93.18$ (2)°, $V = 957.7$ (5) Å^3, $Z = 4$, $D_x = 1.65$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.318$ cm^{-1}, $F(000) = 488$, $T = 298$ K, $R = 0.040$ for 1052 observed reflections. The configuration around

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