ASHKENAZI, P., PELED, M., VOGEL, E. & GINSBURG, D. (1979). *Tetrahedron*, **35**, 1321–1327.
ASHKENAZI, P., VOGEL, E. & GINSBURG, D. (1977). *Tetrahedron*, **33**, 1169–1175.
ASHKENAZI, P., VOGEL, E. & GINSBURG, D. (1978). *Tetrahedron*, **34**, 2167–2169.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
GLEITER, R. & GINSBURG, D. (1979). *Pure Appl. Chem.* **51**, 1301–1315.
KAFTORY, M. (1983). *J. Am. Chem. Soc.* **105**, 3832–3836.
KAFTORY, M. & AGMON, I. (1984). *J. Am. Chem. Soc.* **106**, 7785–7793.
KALO, J., BLOOMFIELD, J. J. & GINSBURG, D. (1978). *Tetrahedron*, **34**, 2153–2155.
KALO, J. & GINSBURG, D. (1978). *Tetrahedron*, **34**, 2155–2160.
KALO, J., VOGEL, E. & GINSBURG, D. (1977*a*). *Tetrahedron*, **33**, 1177–1182.
KALO, J., VOGEL, E. & GINSBURG, D. (1977*b*). *Tetrahedron*, **33**, 1183–1188.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1993). C**49**, 735–738

2,2′-Bis(acetamido)biphenyl

BY J. P. REBOUL

Groupe d'Enseignement et de Recherche en Chimie Thérapeutique, Organique et Physique, Faculté de Pharmacie, 27 *Boulevard Jean-Moulin,* 13385 *Marseille CEDEX* 5, *France*

G. PÈPE AND D. SIRI

CNRS-CRMC2, Campus Luminy, Case* 913, 13288 *Marseille CEDEX* 9, *France*

Y. ODDON

Laboratoire de Chimie Bioorganique, Faculté des Sciences, 33 *rue Louis Pasteur,* 84000 *Avignon, France*

C. CARANONI

Laboratoire de Physique Cristalline associé au CNRS, Unité de Recherche n° 797,
Faculté des Sciences et Techniques Saint-Jérome, Avenue Escadrille Normandie-Niémen,
13397 *Marseille CEDEX* 13, *France*

AND H. RAHAL, J. C. SOYFER AND J. BARBE

Groupe d'Enseignement et de Recherche en Chimie Thérapeutique, Organique et Physique, Faculté de Parmacie, 27 *Boulevard Jean-Moulin,* 13385 *Marseille CEDEX* 5, *France*

(*Received* 18 *March* 1992; *accepted* 23 *September* 1992)

Abstract. 2,2′-Bis(acetylamino)biphenyl, $C_{16}H_{16}N_2O_2$, $M_r = 268.32$, monoclinic, $P2_1/n$, $a = 9.808\ (4)$, $b = 8.780\ (5)$, $c = 17.248\ (6)$ Å, $\beta = 101.70\ (4)°$, $V = 1454.44\ (7)$ Å^3, $Z = 4$, $D_m = 1.21\ (2)$, $D_x = 1.225$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$, $\mu = 6.71$ cm^{-1}, $F(000) = 568$, $T = 293$ K, $R = 0.048$ for 1084 independent reflections. The torsion angle between the phenyl rings is 91.6 (6)°. Conformational parameters are calculated and compared to those of some other 2,2′-biphenyl molecules.

Introduction. The torsion angle between aromatic rings in biphenyl compounds is of great importance for the activity of these molecules on the central nervous system (Shukla, Galy, Brouant, Galy, Soyfer & Barbe, 1985). This angle depends on the nature of substituents branching from the phenyl rings.

To gain some insight on the structure of these compounds, crystal structures of 2-acetamido-2′-diacetamidobiphenyl (ADB) (Reboul, Pèpe, Siri, Oddon, Rahal, Soyfer & Barbe, 1992), 2-nitro-2′-diacetamidobiphenyl (NDB) (Reboul, Rahal, Pèpe, Oddon, Siri, Astier, Soyfer & Barbe, 1992) and of 2,2′-bis(acetamido)biphenyl (BAB) have been investi-

---

* Laboratoire propre du CNRS associé aux Universités d'Aix-Marseille II et III.

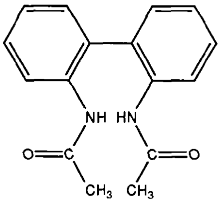
0108-2701/93/040735-04$06.00

Table 1. *Atomic coordinates and equivalent isotropic thermal factors* (Å^2)

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

	x	y	z	B_{eq}
C(1)	0.0857 (5)	0.6993 (6)	0.8444 (3)	2.8 (3)
C(2)	0.0719 (6)	0.5687 (6)	0.8880 (3)	2.8 (2)
C(3)	−0.0587 (7)	0.5050 (8)	0.8848 (4)	3.8 (3)
C(4)	−0.1739 (7)	0.5702 (9)	0.8388 (4)	4.5 (4)
C(5)	−0.1631 (7)	0.7003 (8)	0.7951 (4)	4.6 (4)
C(6)	−0.0331 (7)	0.7641 (7)	0.7990 (3)	4.0 (3)
N(7)	0.1932 (6)	0.5075 (6)	0.9355 (3)	3.4 (3)
C(8)	0.2234 (6)	0.3595 (8)	0.9552 (3)	3.7 (3)
C(9)	0.3617 (8)	0.3337 (9)	1.0073 (5)	5.0 (4)
O(10)	0.1421 (4)	0.2549 (4)	0.9304 (2)	4.6 (2)
C(1′)	0.2253 (5)	0.7654 (6)	0.8404 (3)	2.8 (2)
C(2′)	0.2879 (5)	0.8829 (5)	0.8878 (3)	2.7 (3)
C(3′)	0.4103 (6)	0.9504 (7)	0.8753 (3)	3.6 (3)
C(4′)	0.4706 (7)	0.8963 (7)	0.8147 (4)	4.2 (3)
C(5′)	0.4143 (6)	0.7779 (8)	0.7682 (3)	4.5 (3)
C(6′)	0.2932 (7)	0.7117 (7)	0.7817 (4)	4.4 (3)
N(7′)	0.2255 (5)	0.9414 (6)	0.9496 (3)	3.2 (3)
C(8′)	0.2374 (5)	0.8714 (7)	1.0203 (3)	3.1 (3)
C(9′)	0.1681 (8)	0.9537 (8)	1.0790 (4)	4.4 (3)
O(10′)	0.2990 (4)	0.7512 (4)	1.0358 (2)	4.2 (2)

gated. Crystal features of BAB are reported here, in order to portray more accurately the orientation from one ring to the other when there is substitution in positions 2 and 2′.



BAB

Experimental. The title compound was synthesized in our laboratory (Rahal, 1991). Elongated white prisms were grown from ethanol at 273 K. Density was measured by crystal flotation in water/DMSO solution. The crystal was almost isometric with a mean diameter of 1.4 mm. Lattice parameters were determined by the least-squares procedure applied to the setting angles of 25 strong reflections in the range $0 < \theta < 45°$. Intensity data were measured to $\sin\theta/\lambda = 0.459$ Å^{-1} ($-9 \leq h \leq 9$, $-8 \leq k \leq 8$, $-15 \leq l \leq 15$) with graphite-monochromated Cu $K\alpha$ radiation and $\theta/2\theta$ scans with scan speed of 10° min^{-1} and increment $\Delta\theta = (3.5 + 1.40\tan\theta)°$. Three standards ($\bar{3}3\bar{1}$, $\bar{2}44$ and $\bar{2}3\bar{5}$), measured every hour, showed < 3% variation. Systematic absences proved the space group to be $P2_1/n$. After Lorentz and polarization corrections the initial 9426 reflections were reduced to only 1084 observed data with $I > 3\sigma$. No corrections were made for absorption or extinction. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) with the geometry theoretically defined by *GENMOL* (Pèpe & Siri, 1990) for calculating E values. The structure was refined by full-matrix least squares (181 parameters) with anisotropic temperature factors for non-H atoms and isotropic temperature factors blocked to $U = 0.05$ Å^2 for H atoms placed at theoretical positions. Refinement converged to $R = 0.048$ with $(\Delta/\sigma)_{max} = 0.27$, $S = 0.96$. Scattering factors of Cromer & Mann (1968) were used for C, N, O atoms and values of Stewart, Davidson & Simpson (1965) were used for H atoms. Maximum and minimum heights in the final difference Fourier synthesis were ± 0.27 e Å^{-3}. The function minimized was $\sum w||F_o| - |F_c||^2$ where $w = 1$. All calculations were performed with the *SHELX*76 system (Sheldrick, 1976).

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

C(1)—C(2)	1.393 (7)	C(1′)—C(1)—C(2)	122.2 (4)
C(1)—C(6)	1.387 (7)	C(1′)—C(1)—C(6)	119.0 (4)
C(1)—C(1′)	1.502 (7)	C(2)—C(1)—C(6)	118.7 (5)
C(1′)—C(2′)	1.381 (6)	C(1)—C(1′)—C(2′)	124.2 (4)
C(1′)—C(6′)	1.402 (8)	C(1)—C(1′)—C(6′)	118.3 (4)
C(2)—C(3)	1.389 (8)	C(2′)—C(1′)—C(6′)	117.4 (5)
C(2)—N(7)	1.407 (7)	C(1)—C(2)—C(3)	120.0 (5)
C(2′)—C(3′)	1.394 (7)	C(1)—C(2)—N(7)	117.7 (5)
C(2′)—N(7′)	1.428 (6)	C(3)—C(2)—N(7)	122.2 (5)
C(3)—C(4)	1.368 (9)	C(1′)—C(2′)—C(3′)	121.3 (4)
C(3′)—C(4′)	1.385 (8)	C(1′)—C(2′)—N(7′)	120.3 (4)
C(4)—C(5)	1.384 (9)	C(3′)—C(2′)—N(7′)	118.4 (4)
C(4′)—C(5′)	1.360 (8)	C(2)—C(3)—C(4)	120.1 (6)
C(5)—C(6)	1.382 (9)	C(2′)—C(3′)—C(4′)	118.9 (5)
C(5′)—C(6′)	1.384 (8)	C(3)—C(4)—C(5)	121.1 (6)
C(8)—N(7)	1.360 (8)	C(3′)—C(4′)—C(5′)	121.5 (6)
C(8)—C(9)	1.485 (9)	C(4)—C(5)—C(6)	118.7 (6)
C(8)—O(10)	1.234 (7)	C(4′)—C(5′)—C(6′)	118.8 (5)
C(8′)—N(7′)	1.349 (7)	C(1)—C(6)—C(5)	121.5 (5)
C(8′)—C(9′)	1.513 (8)	C(1′)—C(6′)—C(5′)	122.0 (5)
C(8′)—O(10′)	1.219 (6)	C(9)—C(8)—N(7)	115.0 (5)
		C(9)—C(8)—O(10)	122.9 (5)
		N(7)—C(8)—O(10)	122.1 (5)
		C(9′)—C(8′)—N(7′)	114.8 (5)
		C(9′)—C(8′)—O(10′)	122.5 (5)
		N(7′)—C(8′)—O(10′)	122.7 (5)
		C(2)—N(7)—C(8)	128.7 (5)
		C(2′)—N(7′)—C(8′)	122.6 (4)

C(1)—C(1′)—C(2′)—C(3′)	−172.8 (5)	C(2)—C(3)—C(4)—C(5)	−0.3 (3)
C(1)—C(1′)—C(2′)—N(7′)	5.2 (3)	C(2)—N(7)—C(8)—C(9)	−179.6 (6)
C(1)—C(2)—C(3)—C(4)	0.1 (3)	C(2)—N(7)—C(8)—O(10)	1.4 (3)
C(1)—C(2)—N(7)—C(8)	−148.7 (5)	C(2′)—C(3′)—C(4′)—C(5′)	−1.0 (3)
C(1′)—C(2)—C(1)—C(3)	−174.8 (3)	C(2′)—N(7′)—C(8′)—C(9′)	178.0 (5)
C(1′)—C(2′)—C(3′)—C(4′)	−0.9 (3)	C(2′)—N(7′)—C(8′)—O(10′)	−2.0 (2)
C(1′)—C(2′)—N(7′)—C(8′)	79.7 (4)	C(3)—C(2)—C(1)—C(6)	0.7 (4)
C(2)—C(1)—C(1′)—C(2′)	−96.3 (4)	C(6)—C(1)—C(2)—N(7)	−178.1 (5)
C(2)—C(1)—C(1′)—C(6′)	87.9 (4)		

Discussion. Positional and equivalent isotropic thermal parameters, and the resulting bond lengths and angles, as well as some torsion parameters are reported in Tables 1 and 2.* The atom numbering is given in Fig. 1. The maximum distance of atoms to their mean plane is 0.018 Å. Atoms N(7) and

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes data, bond distances and angles involving H atoms, and a comparison of geometric parameters of biphenyl derivatives have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55701 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1008]

N(7′) are respectively located at −0.029 (5) and −0.002 (5) Å from the mean plane of the rings to which they are connected. Sums of valence angles around the atoms N(7) and N(7′) are close to 360°, indicating sp^2 hybridization for these atoms.

With a view to normalization of the relative position of two planar groups (*X*) and (*Y*), a torsion angle $\tau(X/Y)$ between mean planes of these groups (Reboul *et al.*, 1992) was defined. With reference to this, four mean planes [(*A*) C(1→6); (*B*) C(1′→6′), (*C*) N(7),C(8),C(9),O(10); (*D*) N(7′),C(8′),C(9′),O(10′)] were considered in order to measure deformations induced by atomic strain of the substituent borne by the rings. The $\tau(A/B)$ value is −91.16 (6)°. Values of this torsion angle in related compounds have been calculated: $\tau = 0.0°$ in biphenyl (Charbonneau & Delugeard, 1977), $\tau = 66.7\ (3)°$ in 2,2′-dichlorobiphenyl (Romming, Seip & Aanesen Oymo, 1974), $\tau = 59.1\ (1)°$ in 2,2′-diaminobiphenyl (Ottersen, 1977), $\tau = 83.2\ (4)°$ in biphenyl-2,2′-dicarbonyl chloride (Leser & Rabinovich, 1978), $\tau = 110.1\ (2)$ and 97.1 (2)° in biphenyl-2,2′-dicarboxylic acid, where two independent molecules were observed (Fronczek, Davis, Gehrig & Gandour, 1987).

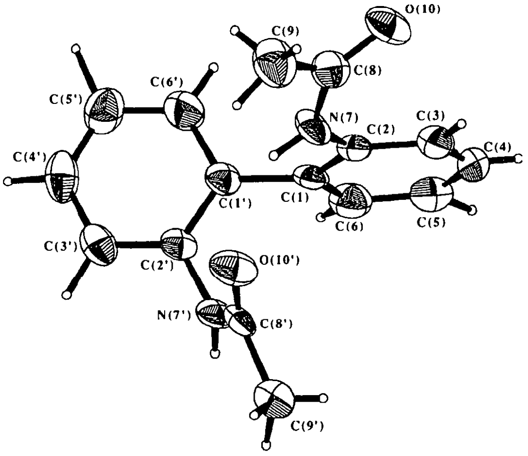


Fig. 1. Molecular view of the title compound drawn using *ORTEP* (Johnson, 1965) with thermal ellipsoids of 50% probability. Spheres representing H atoms have arbitrary radii.

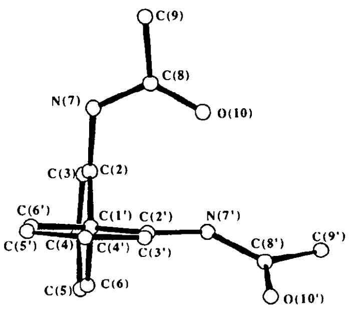


Fig. 2. Projection of the structure along the C(1′)—C(1) bond.

Normally a molecule such as BAB should have a symmetric geometry if there are no strong interactions between ring substituents. Calculations performed on this molecule using the program *GENMOL* indicate a stabilization of the geometry observed. This is a result of weak intramolecular hydrogen bonding [N(7)···O(10′) = 2.814 (5) Å, N(7)—H(7)···O(10′) = 144°], but chiefly results from the coulombic interactions. Strain energy of the symmetric geometry differs from that of the observed geometry by about 8.36 kJ mol^{-1}.

Hence, there are structural analogies between BAB, ADB and NDB derivatives as shown by the torsion angles $\tau(A/B) = -91.1\ (6)$, $\tau(A/C) = 31.6\ (5)$ and $\tau(B/D) = 75.9\ (6)°$ for BAB, $\tau(A/B) = -72.2\ (6)$, $\tau(A/C) = -29.7\ (6)$, $\tau(B/D) = -88.3\ (6)$ and $\tau(B/E) = 119.2\ (7)°$ for ADB, and $\tau(A/B) = 67.1\ (5)$, $\tau(A/C) = 39.8\ (4)$, $\tau(B/D) = 81.1\ (6)$ and $\tau(B/E) = 65.9\ (5)°$ for NDB.

Other deformations can also be noted with respect to the theoretical 120° value of the valence angle of an sp^2 C atom: values of angles C(2)—C(1)—C(6) [118.7 (5)°] and C(2′)—C(1′)—C(6′) [117.4 (5)°] in BAB are decreasing while values of angles C(1′)—C(1)—C(2) [122.2 (4)°] and C(1)—C(1′)—C(2′) [124.2 (4)°] are increasing. A consequence is the non-linearization of the sequence C(4)–C(1)–C(1′)–C(4′), as can be seen in Fig. 2. This phenomenon is a general feature of the 2,2′-disubstituted biphenyl compounds (Ottersen, 1977; Leser & Rabinovich, 1978; Fronczek *et al.*, 1987; Reboul *et al.*, 1992).

The crystal cohesion results from van der Waals interactions. The shortest observed molecular contacts between non-H atoms are O(10)···N(7′^{i}) = 2.871 (7), O(10)···C(5′^{ii}) = 3.363 (8) and C(5′)···O(10^{iii}) = 3.363 (7) Å [symmetry code: (i) $x-1$, $y-1$, z; (ii) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}+z$; (iii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$].

We would like to thank Dr J. P. Astier, Centre de Recherches sur les Mécanismes de la Croissance Cristalline (CRMC2), Université d'Aix-Marseille III, Campus Luminy, Case 913, 13288 Marseille CEDEX 9, France, for valuable technical assistance.

References

Charbonneau, G.-P. & Delugeard, Y. (1977). *Acta Cryst.* **B33**, 1586–1588.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Fronczek, F. R., Davis, S. T., Gehrig, L. M. B. & Gandour, R. D. (1987). *Acta Cryst.* **C43**, 1615–1618.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennesse, USA.

Leser, J. & Rabinovich, D. (1978). *Acta Cryst.* **B34**, 2260–2263.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

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.

Acta Cryst. (1993). C**49**, 738–741

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

By Robert M. Metzger,* Jerry L. Atwood and Wan-Jin Lee

Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487-0336, *USA*

S. M. Rao† and R. B. Lal

Department of Physics, Alabama A and M University, Normal, AL 35762, *USA*

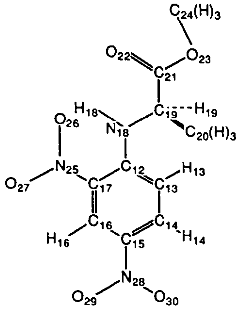
and Boon H. Loo

Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35899, *USA*

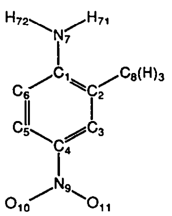
(*Received* 18 *July* 1991; *accepted* 22 *April* 1992)

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}, $\lambda(\text{Mo } K\alpha) = 0.71069$ 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,

---

* To whom correspondence should be addressed.

† Present address: Technical Physics and Prototype Engineering Division, Bhabha Atomic Research Centre, Bombay 400 085, India.

0108-2701/93/040738-04$06.00