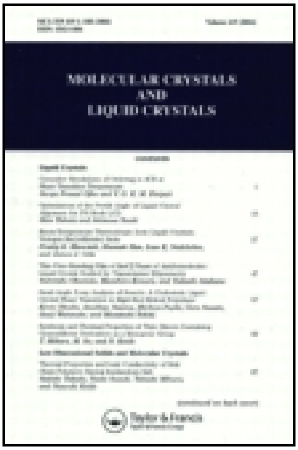

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The Crystal and Molecular Structure and Thermal Properties of the Mesogenic 4″-Nitrophenyl-4-(4′-n-hexyloxybenzoyloxy)-cinnamate; Phase Behavior of Related Compounds

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The Crystal and Molecular Structure and Thermal Properties of the Mesogenic 4″-Nitrophenyl-4-(4′-*n*-hexyloxybenzoyloxy)-cinnamate; Phase Behavior of Related Compounds

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The crystal and molecular structure of the mesogenic 4″-nitrophenyl-4-(4′-*n*-hexyloxybenzoyloxy)-cinnamate, RNO_2, has been determined by X-ray diffraction method. Crystal data: triclinic, space group $P\bar{1}$, $a = 13.570(8)$ Å, $b = 10.885(7)$ Å, $c = 9.805(7)$ Å, $\alpha = 105.34(3)°$, $\beta = 101.17(3)°$, $\gamma = 106.84(3)°$, $Z = 2$. The molecule occurs in its fully extended form, the three phenyl rings are twisted against each other. All molecules lie parallel, the terminal NO_2-groups related to the center of symmetry have a comparatively short NO_2—NO_2' distance, namely, N—N′ = 3.04(1) Å. The thermal behavior of the title compound and related compounds was investigated. The influence of different substituents, Br, CN and a lateral OCH_3 group, on the temperature range of the liquid crystalline phase is discussed.

Keywords: crystalline state, molecular conformation, thermal properties, disubstituted cinnamates

INTRODUCTION

Structural investigations of the solid state of mesogenic compounds give information about the packing and short range ordering in the crystalline state. They are helpful for a better understanding of the relations between the crystalline and liquid crystalline state.[1,2] The X-ray data of various phenyl compounds with end-standing cyano groups revealed that two types of intermolecular contacts in the solid state can occur: (i) the cyano–cyano contact and (ii) the cyano–phenyl contact, both with distances of 3.2–3.7 Å between the neighboring groups.[2–4] These and other reports,[5,6] confirm the important role of strongly dipolar end-groups for the crystal packing as well as for the phase behavior, especially for the formation of an S_A-phase and reentrant phases. Besides the cyano group the nitro group possesses a dipole moment of comparable strength (μ = 4.2 D).[7] The phase transitions in compounds with end-standing nitro groups often show sequences like the cyano containing mesogens, also with a S_A-phase and reentrant behavior.[5,8–10] For some compounds X-ray measurements in the S_A- and nematic phase indicate double layers with ratios *d*/*l* (layer spacing/molecular length) up to 1.25,[9,11] whereas mesogens with cyano–phenyl groups often show a higher *d*/*l* ratio.[12,13]

In this work the crystal and molecular structure of 4″-nitrophenyl-4-(4′-*n*-hexyloxybenzoyloxy)-cinnamate, RNO_2, are presented. The influence of the nitro group on the crystal packing is examined and discussed in respect to packing models for mesogens with end-standing cyano groups. X-ray investigations in the liquid crystalline state of RNO_2 were reported recently.[12] The phase behavior of the title compound is studied together with its cyano and bromo analogues and related compounds with a lateral methoxy group, 4″-(nitro, cyano, bromo)phenyl-4-(4′-*n*-hexyloxybenzoyloxy)-(3-methoxy)-cinnamate.

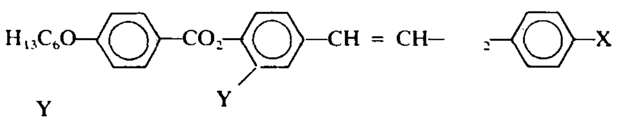
EXPERIMENTAL

Substances and thermal investigations

The compounds investigated are listed in Table I, their syntheses are described elsewhere.[14] The phase transition temperatures were observed using DSC equipment (Du Pont 990) and a polarizing microscope (Leitz Orthoplan Pol) connected with a hot stage (Mettler FP82). Because of a homeotropic alignment of RNO_2 on the normal glass plate a polyimid foil was used to obtain the desired homogeneous

TABLE I

Substances, phase transition temperatures (°C) and heats of transition (kJ/mol) in brackets



Compound	X	Y					
RNO_2†	NO_2	H	C	128[40.1]	S_A	195[#]	N 275[1.5] I
RCN	CN	H	C1	99[9.5]	C2	127[33.7]	N 285[1.7] I
RBr	Br	H	C1	120[6.5]	C2	138[27.5] I S_A 233[#]	N 265[1.5] I
$R'NO_2$	NO_2	OCH_3	C	155[52 .4]	N	194[1.5] I	
R′CN	CN	OCH_3	C	139[34 .4]	N	203[1.9] I	
R′Br	Br	OCH_3	C	137[45 .7]	N	171[1.4]I	

#: is not observable; C: crystalline, S_A: smectic A, N: nematic, I: isotropic.

†Because of the less stability of the sample the observation of the S_A–N transition by optical microscopy is difficult. A clear indication is given by x-ray measurement.[12]

orientation. The transition heats were measured with the DSC equipment. The experimental data are presented in Table I.

Colorless prisms of RNO_2 suitable for X-ray analyses were obtained by slow evaporation of an acetone solution. Intensity measurements were made at 22°C on an automatic STOE-STAD1-4 four-circle-diffractometer with graphite monochromatized MoKα-radiation (λ = 0.71069 Å). The lattice dimensions were determined by a least-squares refinement of 40 strong reflections. The crystal data are:

$C_{28}H_{27}NO_7$, M = 489.5 g·mol^{-1}; triclinic, $P\bar{1}$, a = 13.570(8) Å, b = 10.885(7) Å, c = 9.805(7) Å, α = 105.34(3)°, β = 101.17(3)°, γ = 106.84(3)°, V = 1278.2 Å^3, D_{cald} = 1.27 g·cm^{-3}, Z = 2, F(000) = 516.

For the data collection a crystal of size 0.28*0.15*0.15 mm^3 was mounted parallel to the c-axis. Reflections numbering were measured in the range $3° \leq 2\theta \leq 45°$ (scan $\omega:\theta$ = 1:1) leading to 2825 independent reflections (merging R = 0.0208) of which 2204 had $F_0 > 2\sigma(F_0)$. The standard intensities (400, 012) monitored every 60 min decreased by about 13% during the measurement. LP and absorption corrections were applied ($\mu_{Mo-K\alpha}$ = 0.51 cm^{-1}).

Structure determination and refinement

The structure of RNO_2 was solved by direct methods using the program package SHELX-86,[15] which led to the positions of all non-hydrogen atoms except those of hexyl group. After successive Fourier calculations and isotropic least-squares cycles (program package SHELX-76)[16] the remaining carbon atoms could be located; the refinement with isotropic temperature factors led to R = 0.1960†, with anisotropic temperature factors to R = 0.1344. The hydrogen atoms were geometrically ideally positioned (C—H = 0.96 Å) with fixed isotropic thermal parameters ($U_{iso}(H_{phenyl}) = U_{iso}(H_{acryl})$ = 0.10 Å^2, $U_{iso}(H_{alkyl})$ = 0.15 Å^2). The final refinement with constrained bond lengths for the carbon atoms of the hexyl group (C—C = 1.54(1) Å)[16] converged at R = 0.1160, R_w = 0.0833. The highest difference Fourier peak is 0.42 eÅ^{-3}.

The atomic parameters and equivalent temperature factors for the non-hydrogen atoms are given in Table II. Lists of observed and calculated structure factors, anisotropic thermal parameters and atomic parameters of hydrogen atoms are available from the authors on request.

RESULTS AND DISCUSSION

Thermal properties

Table I shows that the thermal stability of the liquid crystalline phases depends upon the polarity and size of the substituents attached to the main molecular skeleton. Compared with a nitro or cyano group, an end-standing bromine atom having a smaller polarity leads to a decrease of the temperature range of the liquid

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†The R-values are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \Sigma||F_o| - |F_c||*w^{1/2}/\Sigma||F_o||*w^{1/2}$ with $w = k/(\sigma(F_o))^2$ and k from least-squares refinement.

TABLE II

Positional parameters with estimated standard deviations and equivalent temperature factors for RNO_2

$(U_{cq} = 10^3/3(\sum_i \sum_j U_{ij} \cdot a_i^* \cdot a_j^* \cdot (a_i \cdot a_j)/\text{Å}^2)$

Atom	x	y	z	U_{cq}
O(1)	0.3587(7)	1.4143(11)	0.6314(9)	192
O(2)	0.4139(7)	1.6069(8)	0.4545(10)	192
O(3)	0.3221(5)	1.2174(7)	0.980(7)	144
O(4)	0.4845(5)	1.2025(6)	0.0345(6)	110
O(5)	0.2234(3)	0.7263(4)	0.4680(5)	81
O(6)	0.3296(4)	0.8936(5)	0.6828(5)	92
O(7)	0.0982(4)	0.4098(5)	0.8944(7)	131
N(1)	0.3842(8)	1.4845(12)	0.5048(13)	136
C(1)	0.3741(7)	1.4106(12)	0.3939(12)	97
C(2)	0.3897(6)	1.4868(8)	0.2523(13)	99
C(3)	0.3770(6)	1.4208(10)	0.1512(9)	97
C(4)	0.3484(7)	1.2826(11)	0.1952(12)	96
C(5)	0.3342(6)	1.2078(8)	0.3388(12)	105
C(6)	0.3467(6)	1.2733(10)	0.4401(9)	106
C(7)	0.3967(9)	1.1794(8)	0.0252(9)	110
C(8)	0.3418(7)	1.1030(8)	0.0644(9)	110
C(9)	0.3899(6)	1.1030(8)	0.0644(9)	110
C(10)	0.3428(7)	0.9668(7)	0.2270(7)	82
C(11)	0.4059(6)	0.9136(8)	0.3019(8)	98
C(12)	0.3674(7)	0.8351(7)	0.3834(8)	99
C(13)	0.2637(6)	0.8095(7)	0.3834(8)	99
C(14)	0.1982(6)	0.8590(7)	0.3145(8)	91
C(15)	0.2380(7)	0.9387(7)	0.2345(8)	91
C(16)	0.2337(6)	0.7812(9)	0.6183(9)	77
C(17)	0.2169(5)	0.6793(7)	0.6858(8)	66
C(18)	0.2564(5)	0.7203(7)	0.8240(8)	82
C(19)	0.2168(7)	0.6302(8)	0.9106(8)	94
C(20)	0.1424(6)	0.5022(9)	0.8333(10)	91
C(21)	0.1039(6)	0.4611(8)	0.6798(9)	100
C(22)	0.1429(5)	0.5503(7)	0.6091(8)	86
C(23)	0.1328(7)	0.4386(10)	1.0459(10)	157
C(24)	0.0710(10)	0.3005(12)	1.0708(12)	218
C(25)	0.0799(11)	0.2868(20)	1.2177(12)	576
C(26)	0.0008(17)	0.1435(17)	1.1440(14)	511
C(27)	0.0066(12)	0.1541(11)	1.2982(15)	289
C(28)	0.0612(12)	0.0283(15)	1.3225(13)	217

crystalline phase in the order of ~20 K. Besides, the nitro, cyano and bromo substituents which are attached on the p-position of the phenyl lead to a strong dipole moment. Such a dipole may act by attracting the ester or phenyl groups of neighboring molecules and this will tend to increase the smectic and nematic stability.[17,18]. As a result, the liquid crystalline temperature ranges of the R-series are relatively wide (RNO_2: 147 K, RCN: 158 K, RBr: 141 K) and the temperatures of the nematic-isotropic phase transition are high (see Table I). In the R′-series (Table I) a lateral methoxy group is introduced into the molecular skeleton. As a result of increased lateral separation and decreased lateral attraction,[17] the thermal stabilities of the liquid crystalline phase decrease in the order of 80–100 K in comparison with the R-series ($R'NO_2$: 49 K, R′CN: 63 K, R′Br: 34 K). This result

TABLE III

Selected intramolecular bond lengths (Å) and bond angles (°) for RNO_2

O(1)-N(1)	1.201(12)	N(1)-C(1)	1.518(11)
O(2)-N(1)	1.202(11)	C(7)-C(8)	1.517(10)
O(3)-C(4)	1.373(8)	C(8)-C(9)	1.248(8)
O(3)-C(7)	1.351(9)	C(9)-C(10)	1.496(8)
O(4)-C(7)	1.168(9)	C(16)-C(17)	1.488(8)
O(5)-C(13)	1.414(7)	C(23)-C(24)	1.586(8)
O(5)-C(16)	1.363(7)	C(24)-C(25)	1.473(8)
O(6)-C(16)	1.197(7)	C(25)-C(26)	1.497(9)
O(7)-C(20)	1.357(8)	C(26)-C(27)	1.470(9)
O(7)-C(23)	1.390(8)	C(27)-C(28)	1.519(8)
C(7)-O(3)-C(4)	118.3(7)	C(15)-C(10)-C(9)	123.5(8)
C(23)-O(7)-C(20)	120.8(7)	C(12)-C(13)-O(5)	118.7(7)
C(16)-O(5)-C(13)	116.5(5)	C(14)-C(13)-O(5)	119.4(4)
C(1)-N(1)-O(1)	114.9(12)	C(17)-C(16)-O(5)	109.8(7)
C(1)-N(1)-O(2)	115.8(12)	C(17)-C(16)-O(6)	126.5(7)
C(2)-C(1)-N(1)	117.3(11)	O(6)-C(16)-O(5)	123.7(6)
C(6)-C(1)-N(1)	119.6(11)	C(18)-C(17)-C(16)	116.0(7)
O(3)-C(4)-C(3)	119.9(10)	C(22)-C(17)-C(16)	125.3(7)
C(8)-C(7)-O(3)	105.7(9)	C(21)-C(20)-O(7)	115.7(8)
C(8)-C(7)-O(4)	130.7(10)	C(24)-C(23)-O(7)	105.5(3)
O(4)-C(7)-O(3)	123.6(8)	C(25)-C(24)-C(23)	123.6(13)
C(9)-C(8)-C(7)	121.0(9)	C(26)-C(25)-C(24)	88.7(10)
C(10)-C(9)-C(8)	121.6(8)	C(27)-C(26)-C(25)	81.8(10)
C(11)-C(10)-C(9)	118.7(8)	C(28)-C(27)-C(26)	116.6(12)

confirms the theoretical consideration that the length-to-breadth ratio (1/2r) is a useful criterion for the preliminary declaration of phase behavior. A lateral branch breaking up the cylinder shape of the molecules leads to a decrease of the packing fraction[19] in the liquid crystalline phase. For this reason the intermolecular interaction is diminished and furthermore the clearing point should be decreased. From X-ray measurement in the liquid crystalline state we have found, too, that it is difficult for the R′-series to reach a good macroscopic arrangement by use of a magnetic field of ~1 Tesla.

Molecular structure

The molecular structure of RNO_2 is presented in Figure 1, selected bond lengths and angles are given in Table III.

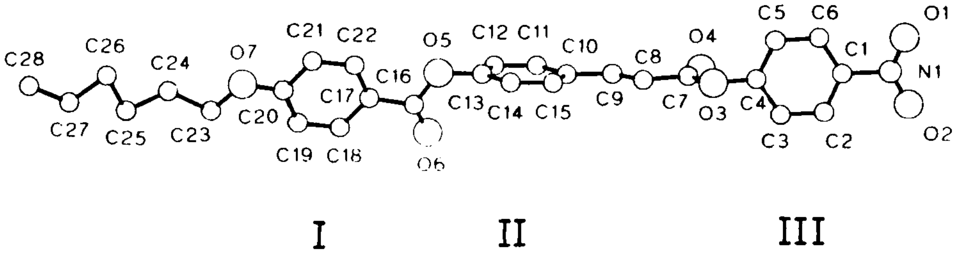

FIGURE 1 Molecular structure of RNO_2 with labeling of the phenyl groups.

The conformation of RNO_2 is determined by the twisted arrangement of the subunits hexyloxybenzoate–cinnamate–nitrobenzene. The dihedral angles τ between best planes of different parts of the molecule are:

$$C_6H_{13}O\text{—}\ \phi_{I}\ \text{—}CO_2\text{—}\ \phi_{II}\text{—}\ C_2H_2CO_2\text{—}\ \phi_{III}\text{—}\ NO_2$$

$$\tau/^\circ \qquad -16.9 \quad -3.2 \quad 70.0 \quad 21.1 \qquad 67.6 \quad 6.9$$

The three phenyl rings show dihedral angles of $\tau(\phi_I/\phi_{II}) = 68.9^\circ$, $\tau(\phi_{II}/\phi_{III}) = -83.8^\circ$ and $\tau(\phi_I/\phi_{III}) = -28.6^\circ$. In related compounds dihedral angles of 49–90° between ϕ–CO_2/ϕ -moieties were observed (e.g. 4′-nitrophenyl-4-octyloxybenzoate, NPOB: 58.1°[20]; 4′-cyanophenyl-4-pentyloxybenzoate, CPPB: 90.0°[21]; 4-butylphenyl-4′butylbenzoylbenzoate: 48.8°, 61.5°[22]; 4′-*n*-pentylphenyl-4′-cyanothiolbenzoate: 69.0°[23]).

The hexyloxy group can only insufficiently be described by a best plane, the maximum of the deviation is 0.70 Å (C(28)). It must be mentioned that this part of the structure is not well resolved, especially the positions of atoms C(25), C(26) and C(27). A statistical disorder in the alkyl chain was not observed. A further influence might be the decrease of the standard intensities during the data collection. The dihedral angle between the OC_6H_{13}-chain and the attached phenyl ring is 16.9°. In NPOB and CPPB the corresponding values are 17°[20] and 0°.[21] The bond distances and angles agree with those observed in analogous structures. However, the distances in the C_6H_{13}-chain lie significantly out of the range for the C—C bond length. Moreover, it should be mentioned that the intensity decrease during the measurements led to higher e.s.d.'s for all distances and angles.

The RNO_2 molecule exists in its "fully stretched" configuration, the distances O(1)–H(C(28)) andO(2)–H(C(28)) are about 29.3 Å including covalent radii[24] (using Van-der-Waal's radii: 31.0 Å).[24] The X-ray data of the liquid crystalline S_A phase and nematic phase revealed a temperature-dependent layer spacing of 33.36 Å (129.5°C) to 36.78 Å (259.4°C) according to a *d*/*l* ratio 1.14–1.26. On this basis a bilayer model for the liquid crystalline phase was proposed.[12]

TABLE IV

Intermolecular atomic distances (Å) in RNO_2. Primed atoms: $-x$, $-y$, $-z$; asterisked atoms: x, $y+1$, $z-1$

Nitro–nitro contacts			
N(1)–N(1)′	3.04(1)	O(1)–O(1)′	3.80(2)
N(1)–O(1)′	3.23(1)	O(2)–O(2)′	3.81(2)
N(1)–O(2)′	3.23(1)	O(1)–O(2)′	3.13(1)
Phenyl rings I/III			
C(1)–C(22)*	3.86(2)	C(3)–C(19)*	3.61(2)
C(2)–C(17)*	3.64(2)	C(3)–C(20)*	3.52(2)
C(2)–C(18)*	3.56(2)	C(4)–C(20)*	4.17(2)
C(2)–C(20)*	3.65(2)	C(4)–C(21)*	4.44(2)
C(2)–C(21)*	3.72(2)		

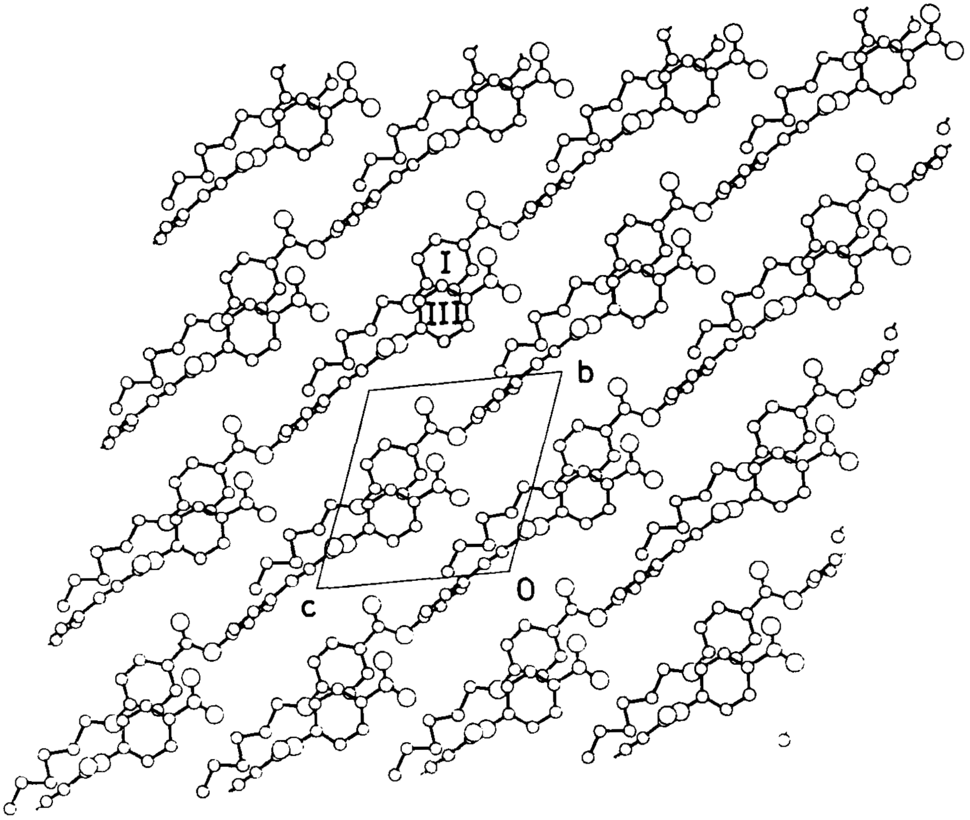

FIGURE 2 Crystal structure of RNO_2, viewed along [100] for the region $-0.07 \leq x \leq 0.5$ (centrosymmetric atoms are omitted).

Molecular packing

Figure 2 shows the arrangement of RNO_2 molecules in the crystalline state, viewed along [100] for $-0.07 \leq x \leq 0.5$ (centrosymmetric atoms are omitted). The molecular long axes are parallel to the [011] diagonal. The distances between carbon atoms of the neighboring phenyl groups I and III (Table IV) vary from 3.56 to 4.44 Å. The projection of the crystal structure along [100] in Figure 3 illustrates the crystal packing caused by the inversion center; here only the nitrophenoxy subunits are plotted ($0 \leq x \leq 1$). The two nitro groups in the unit cell are situated around the inversion center in $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ leading to a compensation of their dipole moments. Their intramolecular distances are listed in Table IV. In comparison with the cyano–cyano′ contacts caused by an inversion center (C—C′ = 3.36–3.50 Å, N—N′ = 3.50–3.55 Å)[3,4] the NO_2—NO_2' distances observed in RNO_2 are rather short (N(1)–N(1)′ = 3.04(1) Å). The sum of the Van-der-Waals radii for two nitrogen atoms is 3.0 Å, for an N, O pair 2.9 Å, respectively.[24] Therefore the distance between these two end-standing groups may be influenced by a weak nitro–nitro′-interaction.

The crystal packing of RNO_2 shows that mesogens with end-standing nitro groups can form "dimeric" units just as reported for cyano–cyano′ contacts.

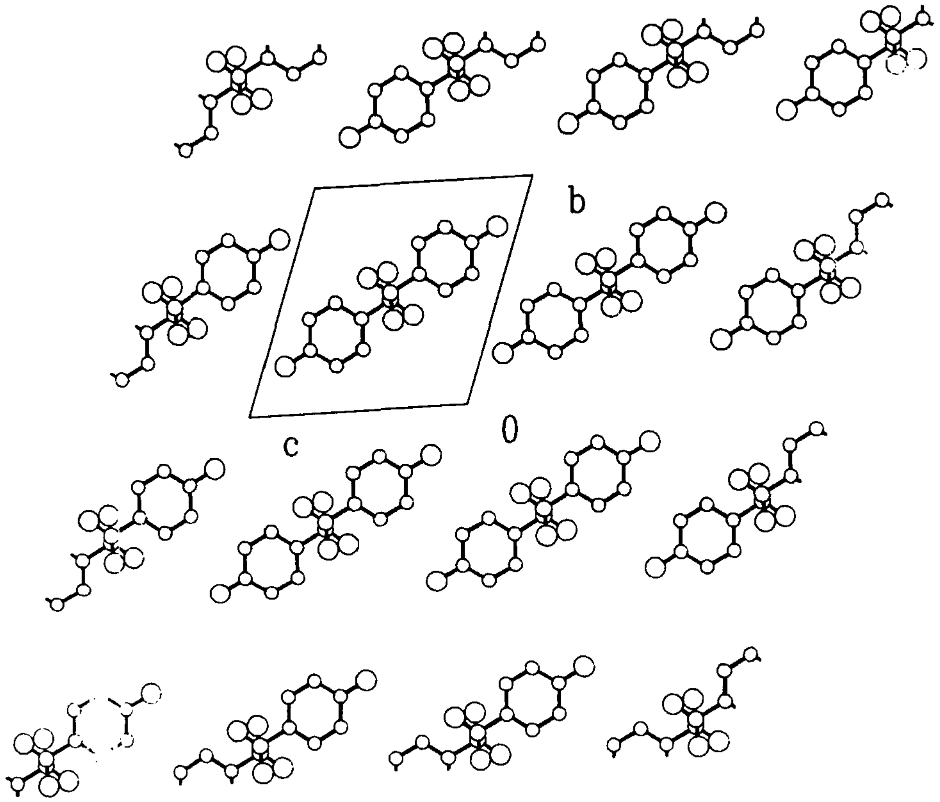

FIGURE 3 Crystal structure of RNO_2, showing the nitro–nitro' contacts. Projection along [100] (only the nitrophenoxy molecular fragments are plotted).

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