and C(9)—N(2) lengths of 1·513 (4) and 1·525 (4) Å reflect the effect of two or more electron-withdrawing groups on the same C atom. In *N,N'*-bis(2,2,2-trinitroethyl)oxamide (Bhattacharjee & Ammon, 1982), for example, a compound containing a $C(NO_2)_3$ group, the average C—N distance is 1·523 (4) Å. Each nitro group is undergoing a strong librational motion about the C—N bond or the central N atom, as evidenced by the large thermal ellipsoids of the O atoms. Consequently, all observed N—O bond lengths are shortened by unknown amounts.

There are no unusual intermolecular contacts.

There is current interest in the prediction of the crystal densities of energetic materials. The values for (I) calculated with the empirical methods of Cady (1979) and Stine (1981) are 1·67 and 1·69 Mg m^{-3}, respectively. The method of Cady calculates a molecular volume by summing the appropriate atom and group-volume increments and includes an empirically derived packing coefficient (unit-cell volume/total molecular volume) to give an effective molecular volume in the crystal, while that of Stine calculates an effective crystal molecular volume from atom and group-volume increments derived from a large structure-density calibration base. A value of 1·63 Mg m^{-3} was obtained with a very simple weight fraction of hydrogen *vs* crystal-density relationship developed several years ago (Ammon, 1980) for use with energetic compounds. The predicted values are in reasonable agreement with the X-ray density of 1·61 Mg m^{-3}, considering that none of the methods was calibrated with cage molecules. Packing calculations, based on the atomic radii listed by Kitaigorodsky (1973), have been carried out for more than 50 C, H, N, O and F containing polynitroorganic compounds (Holden, 1984). The packing coefficients (PC = total molecular volume/unit-cell volume) range from 0·70 in $[FC(NO_2)_2CH_2C(=NH)]_2$ to 0·81 in 2,4,6-trinitro-1,3,5-benzenetriamine. The PC of 0·72 calculated for (I) is at the lower end of the range, suggesting that the compound's crystal density is due, at least in part, to inefficient crystal packing.

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Structure of 7,12-Diphenyl-4a,12-dihydroindeno[7a,1-*b*]naphthalene, $C_{29}H_{22}$

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Abstract. $M_r = 370{\cdot}51$, orthorhombic, *Pbca*, $a = 9{\cdot}968\ (3)$, $b = 17{\cdot}163\ (1)$, $c = 23{\cdot}583\ (2)$ Å, $U = 4034{\cdot}59$ Å^3, $Z = 8$, $D_x = 1{\cdot}22$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}529$ cm^{-1}, $F(000) = 1568{\cdot}00$, $T = 295$ K, $R = 0{\cdot}037$ for 2304 observed reflections. The structure consists of a roughly planar, partly hydro-

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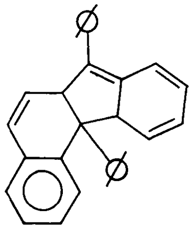
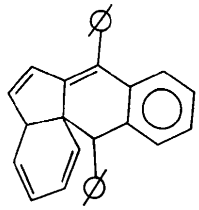
genated fused indenonaphthalene ring system in which the strain imposed by the presence of a carbon atom common to three rings is accentuated by the proximity of a phenyl substituent. The results of the crystallographic investigation are compared with molecular-mechanical calculations.

Introduction. During investigations into the properties of medium-ring annulenes, a compound was isolated (Anastassiou, 1982) which was expected to possess structure (I). The NMR spectrum, however, was not entirely consistent with this expectation (Anastassiou, 1982), and it was in order to shed further light on the matter that the present study was undertaken, revealing the compound as (II).


(I)


(II)

Experimental. Crystal *ca* $0\cdot05\times0\cdot30\times0\cdot38$ mm obtained by room-temperature evaporation of an etheric solution, Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, graphite-crystal-monochromatized Cu $K\alpha$ radiation, 25 reflections ($26<\theta<36°$) used to obtain cell dimensions by least-squares refinement, intensities of 3500 reflections ($0\leq h\leq 11, 0\leq k\leq 19, 0\leq l\leq 26$) measured, $\omega/2\theta$ scan, $\theta_{\max}=60°$; three standard reflections monitored at intervals of 9000 s showed no variation in intensities; 2991 unique and 2304 observed reflections using $I\geq 1\cdot5\sigma(I)$ criterion. Lorentz and polarization corrections applied; direct methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), revealed positions of all non-H atoms. $R_{\rm int}=0\cdot0048$ for merging equivalent reflections. F magnitudes used in E map and full-matrix least-squares refinement of non-H atoms with anisotropic temperature factors, and H atoms (taken from a difference map) isotropically. No absorption correction applied but a secondary-extinction correction ($x=0\cdot00339$ mm^{-1}) reduced R from 0·0402 to 0·0373. Significant improvements were also observed in the standard deviations of some of the bond lengths and angles involving both non-H and H atoms. $R_w=0\cdot045$, weighting scheme for function $w=0\cdot4792/(\sigma^2|F_o|+0\cdot000545F_o^2)$ used to minimize $\sum w\Delta F^2$, $S=0\cdot51$. Max. peak height in final difference Fourier map $=0\cdot151$ e Å^{-3}, ratio of max. LS shift to error 0·075. Form factors for non-H atoms those of Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Calculations on IBM 3033 computer at the University of Petroleum & Minerals using *SHELX*76 (Sheldrick, 1976) programs.

Discussion. Fig. 1 is an *ORTEP* diagram (Johnson, 1976) of the molecule illustrating 30% probability ellipsoids for the non-H atoms and arbitrary spheres of radius 0·1 Å for H atoms together with the crystallographic numbering scheme for the non-H atoms. The crystal packing is shown in Fig. 2. The positional parameters together with their U values for non-H atoms are given in Table 1. Table 2 contains the bond lengths and valence angles involving non-H atoms.*

The core fragment of the title molecule (Fig. 1) consists of a fused tetracyclic entity in which rings A, B, and C are roughly coplanar, with ring D *cis*-fused and disposed pseudo-axially to C. Detailing each ring in turn: ring A is rigorously planar, with bond lengths and angles which are unexceptional; ring B exhibits an approximately planar π-bond system with C(12) and C(13) puckered to either side of this plane by 0·31 and 0·42 Å respectively. The phenyl groups attached to this

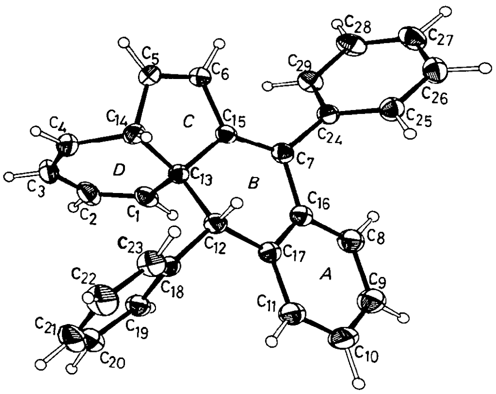


Fig. 1 *ORTEP* diagram of the $C_{29}H_{22}$ molecule.

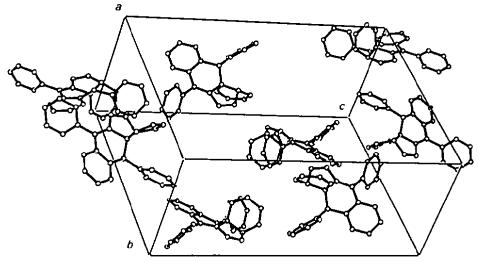


Fig. 2. The unit cell for $C_{29}H_{22}$.

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* Lists of coordinates, bond lengths and angles involving H atoms together with structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39780 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* (×10⁴) (*with e.s.d.'s in parentheses*) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for the non*-H *atoms*

$U_{\text{eq}} = \frac{1}{3}$ (trace of orthogonalized U_{ij} matrix).

	x	*y*	*z*	U_{eq}
C(1)	−212 (2)	3381 (1)	6290 (1)	45
C(2)	−870 (2)	3351 (1)	5799 (1)	57
C(3)	−324 (3)	2955 (1)	5311 (1)	66
C(4)	757 (3)	2506 (1)	5351 (1)	61
C(5)	957 (2)	1600 (1)	6181 (1)	48
C(6)	710 (2)	1670 (1)	6730 (1)	43
C(7)	1064 (2)	2765 (1)	7441 (1)	38
C(8)	1295 (3)	3984 (1)	8017 (1)	52
C(9)	1733 (3)	4741 (1)	8083 (1)	64
C(10)	2370 (3)	5114 (1)	7640 (1)	66
C(11)	2530 (3)	4737 (1)	7128 (1)	54
C(12)	2279 (2)	3542 (1)	6492 (1)	38
C(13)	1105 (2)	2967 (1)	6386 (1)	37
C(14)	1407 (2)	2357 (1)	5915 (1)	45
C(15)	932 (2)	2465 (1)	6917 (1)	36
C(16)	1465 (2)	3589 (1)	7504 (1)	40
C(17)	2069 (2)	3981 (1)	7046 (1)	40
C(18)	2551 (2)	4033 (1)	5971 (1)	39
C(19)	1696 (2)	4633 (1)	5807 (1)	46
C(20)	1889 (3)	5027 (1)	5301 (1)	56
C(21)	2948 (3)	4833 (1)	4955 (1)	67
C(22)	3816 (3)	4248 (2)	5114 (1)	68
C(23)	3626 (2)	3855 (1)	5621 (1)	52
C(24)	906 (2)	2266 (1)	7954 (1)	38
C(25)	−277 (2)	1866 (1)	8062 (1)	46
C(26)	−375 (2)	1382 (1)	8533 (1)	56
C(27)	690 (3)	1299 (1)	8895 (1)	58
C(28)	1867 (3)	1698 (1)	8795 (1)	57
C(29)	1971 (2)	2177 (1)	8328 (1)	48

Table 2. *Bond lengths* (Å) *and angles* (°) *for non*-H *atoms with e.s.d.'s in parentheses*

C(2)–C(1)	1·331 (3)	C(17)–C(12)	1·522 (2)
C(13)–C(1)	1·510 (3)	C(18)–C(12)	1·513 (2)
C(3)–C(2)	1·443 (3)	C(14)–C(13)	1·556 (2)
C(4)–C(3)	1·328 (4)	C(15)–C(13)	1·529 (2)
C(14)–C(4)	1·501 (3)	C(17)–C(16)	1·409 (2)
C(6)–C(5)	1·325 (3)	C(19)–C(18)	1·393 (3)
C(14)–C(5)	1·512 (3)	C(23)–C(18)	1·387 (3)
C(15)–C(6)	1·451 (3)	C(20)–C(19)	1·384 (3)
C(15)–C(7)	1·345 (2)	C(21)–C(20)	1·375 (3)
C(16)–C(7)	1·477 (3)	C(22)–C(21)	1·377 (4)
C(24)–C(7)	1·490 (2)	C(23)–C(22)	1·384 (3)
C(9)–C(8)	1·380 (3)	C(25)–C(24)	1·388 (3)
C(16)–C(8)	1·397 (3)	C(29)–C(24)	1·388 (3)
C(10)–C(9)	1·379 (3)	C(26)–C(25)	1·389 (3)
C(11)–C(10)	1·381 (3)	C(27)–C(26)	1·370 (3)
C(17)–C(11)	1·390 (3)	C(28)–C(27)	1·379 (3)
C(13)–C(12)	1·551 (2)	C(29)–C(28)	1·378 (3)

C(13)–C(1)–C(2)	122·8 (2)	C(7)–C(15)–C(6)	130·8 (2)
C(3)–C(2)–C(1)	121·7 (2)	C(13)–C(15)–C(6)	107·4 (1)
C(4)–C(3)–C(2)	121·4 (2)	C(13)–C(15)–C(7)	121·7 (2)
C(14)–C(4)–C(3)	120·9 (2)	C(8)–C(16)–C(7)	121·3 (2)
C(14)–C(5)–C(6)	112·5 (2)	C(17)–C(16)–C(7)	119·7 (2)
C(15)–C(6)–C(5)	110·8 (2)	C(17)–C(16)–C(8)	119·0 (2)
C(16)–C(7)–C(15)	119·0 (2)	C(12)–C(17)–C(11)	122·4 (2)
C(24)–C(7)–C(15)	121·1 (2)	C(16)–C(17)–C(11)	118·7 (2)
C(24)–C(7)–C(16)	119·8 (1)	C(16)–C(17)–C(12)	118·8 (2)
C(16)–C(8)–C(9)	121·1 (2)	C(19)–C(18)–C(12)	121·8 (2)
C(10)–C(9)–C(8)	119·9 (2)	C(23)–C(18) C(12)	120·0 (2)
C(11)–C(10)–C(9)	119·8 (2)	C(23)–C(18)–C(19)	118·0 (2)
C(17)–C(11)–C(10)	121·5 (2)	C(20)–C(19)–C(18)	121·0 (2)
C(17)–C(12)–C(13)	110·4 (1)	C(21)–C(20)–C(19)	120·0 (2)
C(18)–C(12)–C(13)	111·0 (1)	C(22)–C(21)–C(20)	119·8 (2)
C(18)–C(12)–C(17)	116·5 (1)	C(23)–C(22)–C(21)	120·3 (2)
C(12)–C(13)–C(1)	112·4 (1)	C(22)–C(23)–C(18)	120·8 (2)
C(14)–C(13)–C(1)	112·1 (2)	C(25)–C(24)–C(7)	121·5 (2)
C(14)–C(13)–C(12)	113·4 (2)	C(29)–C(24)–C(7)	119·8 (2)
C(15)–C(13)–C(1)	106·9 (1)	C(29)–C(24)–C(25)	118·6 (2)
C(15)–C(13)–C(12)	108·2 (1)	C(26)–C(25)–C(24)	120·1 (2)
C(15)–C(13)–C(14)	103·1 (1)	C(27)–C(26)–C(25)	120·4 (2)
C(5)–C(14)–C(4)	112·7 (2)	C(28)–C(27)–C(26)	120·0 (2)
C(13)–C(14)–C(4)	115·7 (2)	C(29)–C(28)–C(27)	119·8 (2)
C(13)–C(14)–C(5)	103·0 (1)	C(28)–C(29)–C(24)	121·0 (2)

ring at C(7) and C(12) are oriented at 75·1 and 125·4° respectively to the least-squares plane of *B* and at 54·5° to each other. The phenyl group bonded to the sp^3 centre at C(12) is disposed pseudo-equatorially to *B*. Ring *C* is envelope-shaped, with the 'flap', formed by the intersection of the C(14)—C(13)—C(15) plane with the least-squares plane C(14)—C(5)—C(6)—C(15), at an angle of 17·6°. Ring *D* exhibits a similar, but much flattened, conformation to *B*, with puckering of the sp^3 centres at C(13) and C(14) by 0·10 and 0·26 Å respectively about a plane defined by the diene system C(1)=C(2)—C(3)=C(4).

The strained nature of the fused-ring system is evidenced by the unusually long sp^3—sp^2 bonds at C(13)—C(14) and C(12)—C(13) (1·556 and 1·551 Å respectively), and by the abnormally small values of the C(14)—C(13)—C(15) and C(13)—C(14)—C(5) bond angles (103·1 and 103·0° respectively).

Application of Hirshfeld's (1976) rigid-bond test to the derived thermal-motion tensors indicated that the latter were largely unaffected by absorption phenomena $[\langle(\Delta_{AB})^2\rangle^{1/2} = 0{\cdot}0017\ \text{Å}^2]$, where Δ_{AB} is the difference between the squares of vibration amplitudes along the common vector of atoms bonded together. Analysis of the thermal-motion tensors in terms of a rigid-body model (Schomaker & Trueblood, 1968) resulted in significant disagreement between the observed and calculated tensor components [r.m.s. $\Delta U_{ij} = 0{\cdot}0035\ \text{Å}^2$, $\langle\sigma(U_{ij})\rangle = 0{\cdot}0011\ \text{Å}^2$], largely due to independent librational motion of the two phenyl groups. Exclusion of the phenyl groups from the rigid-body model reduced r.m.s. ΔU_{ij} to 0·0025 Å².

The intermolecular packing arrangement showed no contact less than the sums of the van der Waals radii of the involved atoms.

In view of the considerable skeletal strain in this molecule, it was of interest to compare the results of the crystallographic study with structural parameters calculated using the MMPI force field (Allinger & Yuh, 1976). MMPI is an empirically developed force field which minimizes the overall steric energy by iterative adjustment of the molecular geometry. For conjugated molecules (such as the title compound), a quantum mechanical treatment for the π-MO's is incorporated.

Using the coordinates from Table 1 as input, MMPI smoothly reached a local minimum corresponding to a geometry closely resembling the crystallographic results. Thus, considering only the fused-ring system, the r.m.s. difference in bond lengths between the two studies is 0·011 Å, with the largest difference at C(5)–C(6) where MMPI predicts a bond length longer by 0·023 Å. Similarly, the r.m.s. difference in internal bond angles is 0·9°, with the largest difference at C(5)–C(14)–C(13), where MMPI predicts a bond angle larger by 2·6°. Equally good agreement is found with the torsion angles.

Possible systematic differences in the relative magnitudes of the carbon-atom bond distances and endocyclic angles [$p(i)$] for the fused-ring system derived by the two methods were examined by comparing $\langle [p(i)_{\text{X-ray}} - p(i)_{\text{MMPI}}] \rangle$ with $\langle \sigma p(i) \rangle$. Neither the bond angles nor the 'single'-bond lengths (defined arbitrarily as > 1·40 Å) displayed any systematic variation on this basis. However, there was some indication that the 'double'-bond lengths calculated by MMPI were systematically larger than those obtained from the X-ray data $\{\langle [p(i)_{\text{X-ray}} - p(i)_{\text{MMPI}}] \rangle = -0{\cdot}015$ Å$\}$.

Finally, MMPI predicts orientation of the phenyl groups to each other, and to ring *B* which, within experimental error, are indistinguishable from the crystallographic results.

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Structure of 2-[Hydroxy(methoxycarbonyl)methyl]-2-methoxycarbonyl-4,6-dimethyl-1-phenyl-1,2-dihydropyrimidinium Picrate, $C_{17}H_{21}N_2O_5^+.C_6H_2N_3O_7^-$

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Abstract. $M_r = 561{\cdot}5$, triclinic, $P\bar{1}$, $a = 8{\cdot}113$ (3), $b = 12{\cdot}289$ (2), $c = 13{\cdot}523$ (3) Å, $\alpha = 97{\cdot}20$ (2), $\beta = 105{\cdot}67$ (2), $\gamma = 89{\cdot}11$ (2)°, $V = 1287{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}45$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}114$ cm^{-1}, $F(000) = 584$, $T = 290$ K, $R = 0{\cdot}051$ for 2161 observed reflexions. The structure of the title compound has been established, thus confirming the occurrence of ring expansion in its synthesis by reaction of 1-[1,2-bis(methoxycarbonyl)-1-vinyl]-3,5-dimethyl-2-phenylpyrazolium tetrafluoroborate with alkali. Bond lengths and angles are normal. Two asymmetrically bifurcated hydrogen bonds link the anion to the cation.

Introduction. By reaction of 1-[1,2-bis(methoxycarbonyl)-1-vinyl]-3,5-dimethyl-2-phenylpyrazolium tetrafluoroborate with alkali, a mixture of two diastereoisomeric dihydropyrimidines is obtained: (*RR,SS*) and (*RS,SR*)-2-[hydroxy(methoxycarbonyl)methyl]-2-methoxycarbonyl-4,6-dimethyl-1-phenyl-1,2-dihydropyrimidine. Afterwards, this mixture was treated with acid and it was observed through ^{1}H NMR spectroscopy that only one of the two possible diastereoisomeric salts was formed (Elguero, de la Hoz & Pardo, 1984).

We have determined the crystal structure of the title compound in order to establish the molecular structure of the compound and thus the nature of the expansion in the pyrazole ring, and also to establish the stereochemistry of the salt obtained as a product of the reaction with acid.

Experimental. Clear colourless, prismatic crystal 0·5 × 0·2 × 0·3 mm. Enraf–Nonius CAD-4F automatic diffractometer, cell dimensions refined by least-squares fitting of θ values of 25 reflexions; intensities of 5591 unique reflexions, $1 < \theta < 27°$, *hkl*

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