January, 1994] *Bull. Chem. Soc. Jpn.*, ***67***, *31—38(1994)* 31

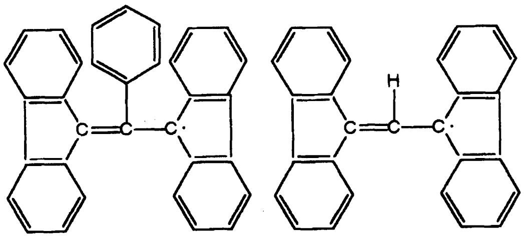
Molecular and Crystal Structures of Complexes of Stable Free Radical BDPA with Benzene and Acetone

Nagao AZUMA,* Takehiro OZAWA, and Jun YAMAUCHI†
Department of Chemistry, Faculty of General Education, Ehime University, Matsuyama 790
†Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606
(Received July 15, 1993)

The crystal structures of two complexes of the 9-(9*H*-fluoren-9-ylidenephenylmethyl)-9*H*-fluoren-9-yl stable radical with benzene (BDPA–Bz) and acetone (BDPA–Ac) have been determined by X-ray diffraction at room temperature. They are an isostructure of a monoclinic system with a space group of $P2_1/n$. For BDPA–Bz, a=9.502(2), b=14.632(2), c=19.452(2) Å, β=93.64(1)°, V=2699(1) Å^3, Z=4, D_x=1.220 g cm^{-3}. For BDPA-Ac, a=9.657 (1), b=14.675(2), c=18.812(2) Å, β=95.388(9)°, V=2654.4(6) Å^3, Z=4, D_x=1.190 g cm^{-3}. The final R values are 0.043 and 0.062 for 5.47 and 3.93 ratio of the observed reflections versus the parameters for BDPA–Bz and BDPA–Ac, respectively. The BDPA molecules in both crystals have the same propeller shape with an approximated C_2 symmetry. The molecular packing of these crystals does not show a one-dimensional stacking, in spite of the magnetic one-dimensionality elucidated by the magnetic susceptibilites. The exchange pathways are discussed based on the McConnell's spin-density Hamiltonian.

The aromatic free radical 9-(9*H*-fluoren-9-ylidenephenylmethyl)-9*H*-fluoren-9-yl, which has been considered as a derivative of the allyl radical and is called 1,3-bisdiphenylene-2-phenyl-allyl (BDPA) in the literature, forms a 1 : 1 complex with benzene.[1)] BDPA is remarkably stable to oxygen, and is highly dissociative or does not tend to dimerize, which may be partly attributed to a delocalization of the unpaired electron over the entire molecular framework and partly to a steric hindrance. However, there is little information concerning its molecular geometry, because, unlike 9-(9*H*-fluoren-9-ylidenemethyl)-9*H*-fluoren-9-yl (BDA), since BDPA has no hydrogen atom on the internal allylic chain (Scheme 1) the ESR and ENDOR technique are only little effective. Therefore, it is interesting to determine the molecular structure of this radical.

This radical has been subjected to extensive magnetic studies.[2—4)] It has been indicated based on several magnetic measurements that BDPA is a one-dimensional antiferromagnet with a Heisenberg-type isotropic exchange interaction of $J/k=-4.4$ K.[3,4)] BDPA is probably the first free radical crystal whose magnetic phase transition from a paramagnetic to an antiferromagnetic state at 1.695 K has been indicated.[3)] This phase transition can be attributed to a significant interchain exchange coupling. Yamauchi and Deguchi have estimated the interchain exchange parameter to be $|J'/k|=0.04|J/k|=0.18$ K based on a two-dimensional interchain interaction, which indicates quasi-one-dimensionality.[5)] Detailed knowledge concerning the molecular structure, spin-density distribution, and crystal structure is indispensable for understanding the magnetic properties. However, the X-ray diffraction of BDPA has not been reported since its discovery, probably because of difficulty in obtaining suitable crystals for diffraction. We have crystalized 1 : 1 complexes of BDPA with benzene (BDPA–Bz) and acetone (BDPA–Ac) of good quality. In this paper we describe the molecular and crystal structures of these radicals. It is noted that the BDPA molecule has no hetero atom, unlike many other stable radicals with a delocalized π-spin. This may be advantageous for estimating the spin-density distribution based on simple molecular orbital (MO) theories; the calculated spin densities of BDPA radical are also presented.



BDPA BDA

Scheme 1.

Experimental

Material Preparation. BDPA was prepared according to the procedures of Koelsch[1)] as well as Kuhn and Neugebauer.[6)] The crystals used for the diffraction were obtained by repeated careful recrystallization from benzene and acetone solution at ambient temperature.

Structure Determination. Suitable crystals of BDPA–Bz and BDPA–Ac were mounted on an automated four-circle diffractometer (Rigaku AFC5R) equipped with graphite-monochromatized Cu $K\alpha$ radiation (λ=1.5418 Å) from a fine-focus anode of 12 kW-type rotating-anode generator. The cell dimensions of both crystals were obtained by using the respective 25 reflections (51°<2θ<55°) at 25 °C; the results appear in Table 1. By using the ω–2θ scan mode with a scan rate 16° min^{-1} (in ω), intensity measurements of unique reflections of both crystals were undertaken from 4.7° to 123° in 2θ. Two rescans were applied for weak reflections. The ranges of the scan were $\Delta\omega=(\omega_o+0.30\ \tan\ \theta)°$ with $\omega_0=1.52$ for BDPA–Bz and $\omega_o=1.63$ for BDPA–Ac. Corrections were made for the Lorentz and polarization fac-

Table 1. Crystal Data, Experimental Conditions, and Refinement Details of BDPA–Bz and BDPA–Ac

	BDPA–Bz	BDPA–Ac
Empirical formula	$C_{33}H_{21}\cdot C_6H_6$	$C_{33}H_{21}\cdot C_3H_6O$
Formula weight	495.64	475.61
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	9.502(2)	9.657(1)
b/Å	14.632(2)	14.675(2)
c/Å	19.452(2)	18.812(2)
β/°	93.64(1)	95.388(9)
V/Å^3	2699(1)	2654.4(6)
Z	4	4
D_x/g cm^{-3}	1.220	1.190
μ(Cu $K\alpha$)cm^{-1}	4.89	5.03
Crystal size/mm	0.35×0.20×0.05	0.38×0.18×0.40
Range of 2θ/°	4.7—123.0	4.7—123.1
No. of reflections measured	4668	4589
No. of unique reflections (R_{int})	4376 (0.065)	4305 (0.072)
No. of reflections obsd. ($I>3\sigma(I)$)	1931	1316
Reflections/parameter ratio	5.47	3.93
R, R_w	0.043, 0.040	0.062, 0.059
S (goodness of fit)	1.35	1.97
Maximum shifts/error	0.01	0.02
Residual electron density/e Å^{-3}	−0.17—0.18	−0.17—0.25

tors. Three standard reflections monitored at every 150 reflections showed an intensity deterioration down to 96.3 % of the initial values of BDPA–Ac. A falling-off of the intensities with the elapse of time was corrected based on the linear decay in the standard reflections. Empirical corrections for the absorption were made based on azimuthal (Ψ) scans of the respective five reflections.[7] The structures were solved by the direct method using the MITHRIL program.[8] The coordinates and anisotropic thermal parameters for the non-hydrogen atoms were refined by a full-matrix least-squares procedure based on F with the weight $w=1/\sigma^2(F_o)$. The positions of the hydrogen atoms were idealized (C-H 0.95 Å), assigned isotropic thermal parameters $B(\mathrm{H})=1.2B_{\mathrm{eq}}(\mathrm{C})$ and allowed to ride on their parent carbons. All of the calculations were carried out on a VAX station 3200 computer with TEXSAN programs,[9] which used the atomic scattering factors taken from "International Tables for X-Ray Crystallography"[10] and took anomalous dispersion into account. The refinement details are shown in Table 1, where the secondary extinction coefficient (0.13×10^{-5} for BDPA–Bz and 0.16×10^{-5} for BDPA–Ac) was included in the variables. The final atomic parameters for the non-hydrogen atoms are given in Tables 2 and 3.[11] All of the measurements and calculations were carried out at the Advanced Instrumentation Center for Chemical Analysis, Ehime University.

Results and Discussion

The space group of BDPA–Bz is the same as that of BDPA–Ac and the cell dimensions of these crystals are also similar to each other. This implies that both crystals have a common structure of the BDPA molecule and similar cavities to accommodate benzene and acetone guests. Actually, we have found little significant difference in the molecular structures between the two BDPA molecules. Therefore, we describe only the molecular structure of BDPA in the BDPA–Bz crystal.

Thermal ellipsoids with the atomic numbering of the BDPA molecule in the BDPA–Bz crystal are shown in Fig. 1. Quite the same numbering scheme is adopted for BDPA in the BDPA–Ac crystal.

Molecular Structure of BDPA. The internal

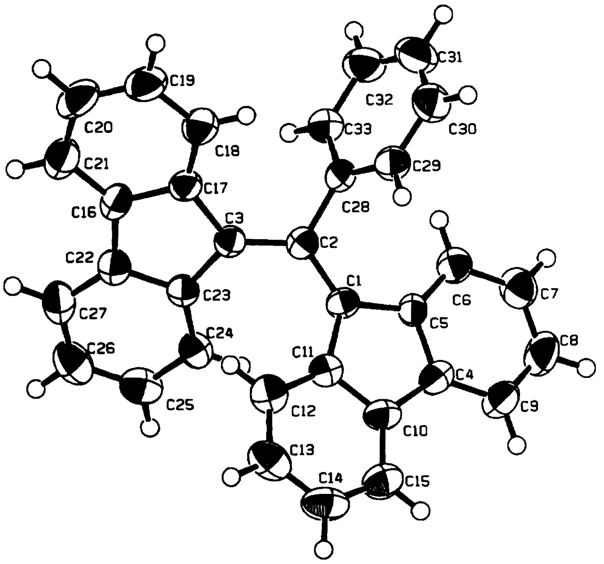


Fig. 1. ORTEP drawing of the BDPA molecule in the BDPA–Bz crystal and the atomic numbering scheme. Quite the same numbering system is adopted for the BDPA–Ac crystal.

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors (B_{eq}) of BDPA–Bz with esd's in Parentheses, and McLachlan π-Spin Densities

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^{2\mathrm{a})}$	Spin density
C(1)	0.6455(4)	0.2869(2)	0.3153(2)	3.1(2)	0.25989
C(2)	0.5190(4)	0.2379(2)	0.3181(2)	3.1(2)	−0.07355
C(3)	0.4507(3)	0.1902(2)	0.2629(2)	3.0(2)	0.25989
C(4)	0.8277(4)	0.3913(3)	0.3429(2)	3.6(2)	0.05061
C(5)	0.6903(4)	0.3660(2)	0.3585(2)	2.9(2)	−0.02373
C(6)	0.6195(4)	0.4193(2)	0.4050(2)	3.7(2)	0.06964
C(7)	0.6871(5)	0.4944(3)	0.4349(2)	4.8(2)	−0.01214
C(8)	0.8231(5)	0.5169(3)	0.4205(2)	5.5(3)	0.05941
C(9)	0.8944(4)	0.4662(3)	0.3739(2)	4.8(2)	−0.00200
C(10)	0.8743(4)	0.3282(3)	0.2905(2)	3.7(2)	0.05061
C(11)	0.7644(4)	0.2665(2)	0.2733(2)	3.2(2)	−0.02373
C(12)	0.7879(4)	0.1970(3)	0.2263(2)	4.1(2)	0.06964
C(13)	0.9167(5)	0.1921(3)	0.1969(2)	4.7(2)	−0.01214
C(14)	1.0210(4)	0.2552(3)	0.2129(2)	5.2(2)	0.05941
C(15)	1.0017(4)	0.3238(3)	0.2604(2)	4.6(2)	−0.00200
C(16)	0.3004(4)	0.0890(2)	0.2004(2)	3.4(2)	0.05061
C(17)	0.3540(3)	0.1120(2)	0.2670(2)	3.3(2)	−0.02373
C(18)	0.3183(4)	0.0583(3)	0.3228(2)	4.4(2)	0.06964
C(19)	0.2265(5)	−0.0147(3)	0.3106(2)	5.2(2)	−0.01214
C(20)	0.1716(4)	−0.0350(3)	0.2453(3)	5.6(3)	0.05941
C(21)	0.2081(4)	0.0164(3)	0.1892(2)	4.8(2)	−0.00200
C(22)	0.3576(4)	0.1532(2)	0.1515(2)	3.4(2)	0.05061
C(23)	0.4490(3)	0.2128(2)	0.1892(2)	3.0(2)	−0.02373
C(24)	0.5115(4)	0.2843(2)	0.1549(2)	3.6(2)	0.06964
C(25)	0.4867(4)	0.2924(3)	0.0845(2)	4.4(2)	−0.01214
C(26)	0.3990(5)	0.2317(3)	0.0479(2)	5.1(2)	0.05941
C(27)	0.3318(4)	0.1623(3)	0.0812(2)	4.5(2)	−0.00200
C(28)	0.4504(4)	0.2395(2)	0.3851(2)	3.2(2)	0.00200
C(29)	0.5265(4)	0.2193(2)	0.4457(2)	3.9(2)	−0.00545
C(30)	0.4666(5)	0.2271(3)	0.5088(2)	5.2(2)	0.00014
C(31)	0.3293(6)	0.2545(3)	0.5099(2)	5.9(3)	−0.00478
C(32)	0.2494(4)	0.2730(3)	0.4509(2)	5.2(2)	0.00014
C(33)	0.3110(4)	0.2653(3)	0.3881(2)	4.0(2)	−0.00545
C(41)	0.8992(5)	0.0682(3)	0.4245(3)	7.1(3)	
C(42)	0.8724(7)	0.0512(4)	0.3570(3)	7.8(4)	
C(43)	0.756(1)	0.0021(5)	0.3357(3)	9.9(5)	
C(44)	0.6682(8)	−0.0306(4)	0.3834(5)	10.0(5)	
C(45)	0.6965(7)	−0.0126(4)	0.4514(4)	8.0(4)	
C(46)	0.8133(7)	0.0359(4)	0.4720(3)	7.5(3)	

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

allylic structure is fairly planar; the atomic deviations of C(2), C(5), C(11), C(17), C(23), C(29), C(31), and C(33) from the plane, defined by C(1), C(3), and C(28), are 0.013, −0.534, 0.595, 0.511, −0.640, 0.895, −0.137, and −0.948 Å, respectively; the estimated standard deviations (esd) are 0.003—0.004 Å. The same atomic deviations in BDPA–Ac are −0.00, −0.51, 0.69, 0.53, −0.63, 0.96, 0.07, and −0.91 Å; the esd's are 0.009—0.01 Å. Two fluorenyl and phenyl moiety are arranged in a propeller shape. The torsion angle of the C(1)-fluorenyl blade is 29°, which is the average of the dihedral angles between the C(3)–C(2)–C(1) and C(2)–C(1)–C(5) planes and between C(3)–C(2)–C(1) and C(2)–C(1)–C(11) planes. The same angle of the counterpart C(3)-fluorenyl blade is 30°. Both of the same torison angles in BDPA–Ac are 30°. The equivalency between the two blades is also observed in the bond distances and angles; they agree well with the corresponding counterpart(s) within the experimental accuracy, as shown in Tables 4 and 5. Therefore, the point group of the BDPA molecule in these crystals is safely approximated as C_2 symmetry. Two phenylenes and an internal cyclopentadiene ring in the fluorenyl moiety are coplanar within the individual rings. The fluorenyl moieties are of the chair form; the planes of C(4)—C(9)- and C(10)—C(15)-phenylene bend up- and downward, respectively, from the internal cyclopentadiene plane by 2°—3°. The same degree of bending have been observed in other fluorenyl moiety and two fluorenyl moieties in BDPA–Ac. A detailed examination

Table 3. Atomic Coordinates and Equivalent Isotropic Temperature Factors (B_{eq}) of BDPA–Ac with esd's in Parentheses

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$ a)
C(1)	0.4507(8)	0.1820(6)	0.2695(5)	4.4(5)
C(2)	0.5149(8)	0.2332(6)	0.3258(4)	3.7(4)
C(3)	0.6395(8)	0.2830(6)	0.3215(4)	3.5(4)
C(4)	0.305(1)	0.0800(8)	0.2038(7)	5.7(6)
C(5)	0.3579(9)	0.1024(6)	0.2749(6)	5.1(6)
C(6)	0.328(1)	0.0493(8)	0.3332(6)	7.1(7)
C(7)	0.241(1)	−0.0254(8)	0.3199(8)	9.0(9)
C(8)	0.189(1)	−0.048(1)	0.254(1)	9(1)
C(9)	0.218(1)	0.005(1)	0.1949(7)	8(1)
C(10)	0.357(1)	0.1440(7)	0.1540(6)	5.2(6)
C(11)	0.4445(9)	0.2042(7)	0.1924(5)	4.5(5)
C(12)	0.5009(9)	0.2757(7)	0.1563(5)	5.1(6)
C(13)	0.473(1)	0.2828(7)	0.0831(6)	6.7(7)
C(14)	0.386(1)	0.221(1)	0.0461(6)	8.4(9)
C(15)	0.323(1)	0.1506(9)	0.0807(7)	7.1(8)
C(16)	0.8161(9)	0.3894(6)	0.3450(5)	4.1(5)
C(17)	0.6841(8)	0.3650(6)	0.3630(4)	3.5(5)
C(18)	0.6136(8)	0.4208(6)	0.4081(5)	4.1(5)
C(19)	0.678(1)	0.4982(7)	0.4350(5)	5.0(6)
C(20)	0.813(1)	0.5213(7)	0.4198(5)	6.2(7)
C(21)	0.880(1)	0.4668(7)	0.3742(6)	5.6(6)
C(22)	0.8624(9)	0.3237(6)	0.2955(4)	4.0(5)
C(23)	0.7570(9)	0.2595(6)	0.2811(4)	3.8(5)
C(24)	0.779(1)	0.1862(7)	0.2371(5)	5.4(6)
C(25)	0.908(1)	0.1782(8)	0.2094(5)	6.4(6)
C(26)	1.008(1)	0.2438(9)	0.2224(5)	6.5(7)
C(27)	0.986(1)	0.3156(7)	0.2661(5)	5.7(6)
C(28)	0.447(1)	0.2363(6)	0.3946(5)	4.1(5)
C(29)	0.310(1)	0.2610(6)	0.3936(5)	5.1(6)
C(30)	0.248(1)	0.2660(7)	0.4561(6)	5.9(6)
C(31)	0.326(1)	0.2482(7)	0.5194(6)	7.1(7)
C(32)	0.461(1)	0.2240(7)	0.5201(5)	6.6(6)
C(33)	0.5225(9)	0.2184(6)	0.4590(5)	4.9(5)
O(1)	0.788(2)	0.031(1)	0.4798(8)	22(1)
C(41)	0.807(3)	0.029(2)	0.416(1)	16(2)
C(42)	0.708(2)	−0.014(1)	0.368(1)	22(2)
C(43)	0.931(2)	0.063(2)	0.395(1)	17(2)

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

of these bends shows that the bends of two phenylene rings from the internal cyclopentadiene plane point in directions which are effective for reducing the inter-blade repulsions. This seems to be quite reasonable, because the repulsion energies due to bulky substituents are relieved by distribution into two types of freedom: twisting and bending. Actually, the torsion angle of the phenyl blade, which has little freedom of bending within the ring system, is 51° (52° in BDPA–Ac). This implies a reduced π-conjugation between the allyl and phenyl moieties.

In order to estimate the effect of π-conjugation, the bond orders (P_{rs}) of the various bonds are considered; the definition is

$$P_{rs}=1+\Sigma n_i C_{ri} C_{si}, \tag{1}$$

where n_i is the number of π-electrons in the i-th π-molecular orbital (MO), and C_{ri} and C_{si} are the orbital coefficients of the r and s atomic orbital in the i-th MO. Various relationships between the bond order and length have been developed; in the present paper the formula of Jenkins are employed after Fischer:[12)]

$$1/d_{\mathrm{cc}}^2=0.2868+0.1334P_{rs}, \tag{2}$$

where d_{cc} is the observed C–C bond distance. We obtained observed bond orders of 1.66 for the C(2)–C(1) and C(2)–C(3) bonds. This value is the same as that for the C–C bonds in benzene, where 1.67 is expected. This value is somewhat smaller than 1.71 and 1.69, which were calculated for the allyl radical based on HMO[13)] and UHF[14)] calculations, respectively. On the other hand, the average of the observed bond orders for the C(1)–C(5), C(1)–C(11), C(3)–C(17), and C(3)–C(23) bonds is 1.31, while that for C(4)–C(10) and C(16)–C(22) is 1.34. That for the C(2)–C(28) bond is 1.21, which is similar (or smaller) rather than 1.25—1.24 for the corresponding C–Ph bond in verdazyl radicals, where the torsion angle is about 2°[15)] and where the phenyl group, like that in BDPA, is attached to the nodal carbon atom in respect to the singly occupied

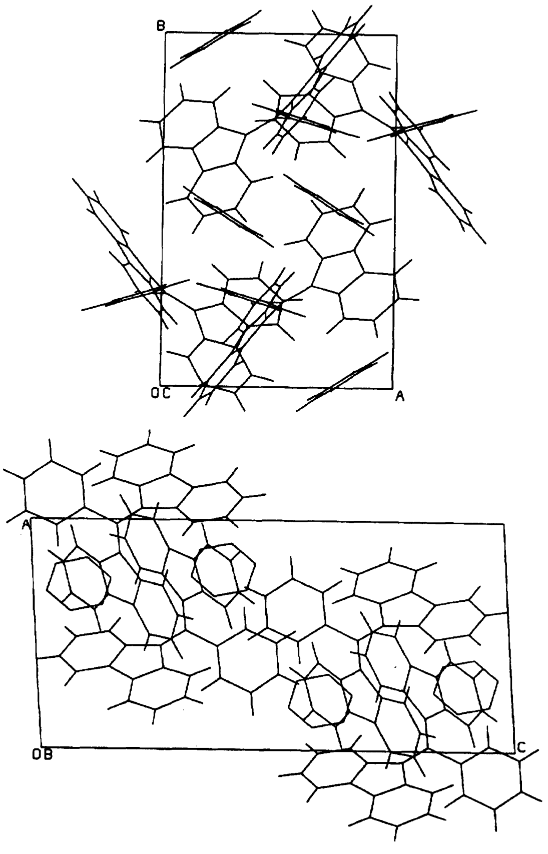


Fig. 2. Molecular packing in the unit cell of the BDPA–Bz crystal. Top: ab-plane view. Bottom: ac-plane view. The hydrogen atoms of the benzene in the ac-plane view are omitted for clarity.

Table 4. Selected Bond Distances (l) in BDPA–Bz (**Bz**) and BDPA–Ac (**Ac**) Crystal with esd's in Parentheses

Bond	**Bz** l/Å	**Ac** l/Å	Bond	**Bz** l/Å	**Ac** l/Å
C(1)–C(2)	1.403(4)	1.39(1)	C(2)–C(3)	1.404(4)	1.42(1)
C(2)–C(28)	1.494(4)	1.51(1)	C(1)–C(5)	1.477(4)	1.48(1)
C(1)–C(11)	1.467(4)	1.48(1)	C(4)–C(5)	1.409(4)	1.43(1)
C(10)–C(11)	1.405(5)	1.38(1)	C(4)–C(10)	1.464(5)	1.45(1)
C(3)–C(17)	1.473(4)	1.48(1)	C(3)–C(23)	1.470(4)	1.46(1)
C(16)–C(17)	1.403(4)	1.40(1)	C(22)–C(23)	1.404(4)	1.39(1)
C(16)–C(22)	1.466(5)	1.44(1)			

Table 5. Selected Bond Angles (ϕ) in BDPA–Bz (**Bz**) and BDPA–Ac (**Ac**) Crystal with esd's in Parentheses

Bond	**Bz** ϕ/°	**Ac** ϕ/°
C(1)–C(2)–C(3)	125.4(3)	123.7(8)
C(1)–C(2)–C(28)	116.6(3)	118.1(7)
C(3)–C(2)–C(28)	118.0(3)	118.2(7)
C(2)–C(1)–C(5)	126.5(3)	127.0(9)
C(2)–C(1)–C(11)	127.6(3)	126.7(9)
C(5)–C(1)–C(11)	105.8(3)	105.8(8)
C(1)–C(5)–C(4)	108.7(3)	106(1)
C(5)–C(4)–C(10)	108.1(3)	110(1)
C(4)–C(10)–C(11)	108.6(3)	108(1)
C(10)–C(11)–C(1)	108.9(3)	110(1)
C(2)–C(3)–C(17)	127.1(3)	126.7(8)
C(2)–C(3)–C(23)	127.6(3)	127.7(8)
C(17)–C(3)–C(23)	105.0(3)	105.3(7)
C(3)–C(17)–C(16)	109.1(3)	107.9(8)
C(17)–C(16)–C(22)	108.5(3)	109.4(8)
C(16)–C(22)–C(23)	107.5(3)	108.2(8)
C(22)–C(23)–C(3)	109.7(3)	109.1(8)

molecular orbital (SOMO). The C(2)–C(28) bond order of 1.21 is apparently smaller than 1.34 for those of the C(4)–C(10) and C(16)–C(22) bonds. These values show that the BDA skeleton is a delocalized π-electron framework, but that the π-electrons on the phenyl group at C(2) incline so as to localize within this ring. Watanabe et al.[16)] reported, based on ESR and ENDOR studies for the solution, that the fluorenyl blades in BDA were twisted by 37°, and suggested the same twisted angle for BDPA. This angle is in good accordance with the value of 30° observed for the crystal.

Molecular Orbital Calculation. In order to estimate the bond orders and π-spin densities, molecular orbital calculations due to Hückel[13)] and McLachlan[18)] were performed. In these calculations, the following parameters, the symbols of which have their usual meanings, are employed: $\lambda=1.2$, $\beta=\beta_C \cos\theta$, and $\theta=30°$, 30°, and 50° for the torsion angles around the C(1)–C(2), C(2)–C(3), and C(2)–C(28) bond, respectively. The planarity of the fluorenyl moieties is assumed. The calculated bond orders for the C(1)–C(2) and C(2)–C(28) bonds are 1.58 and 1.21, respectively, which are consistent with those obtained from the bond distances, 1.66 and 1.21. However, the observed bond orders for the C(1)–C(5) and C(4)–C(10) bonds of 1.31 and 1.34 are reversed in the present calculation: 1.46 and 1.40.

The π-electron charge densities on the C(1) and C(2) atoms are 0.986, 0.911, respectively, which is evidence for delocalization of the π-electrons, while allyl radical gives a unit charge density on every carbon atom. The delocalization stabilizes the SOMO level down to 0.18β, unlike zero of the allyl radical.

The McLachlan spin densities calculated for the BDPA radical are shown in Table 2. About 0.5 of the π-spin density is distributed on the allyl group and the residual 0.5 on the 2,2′-biphenylydiyl groups. The spin density on the phenyl blade is, accordingly, very small; the negative spin density is dominant in this blade. The reproducibility of the proton hyperfine coupling constants estimated from the ESR and ENDOR spectrum of BDPA in solution is of the same level as that of Watanabe et al.[16)]

Crystal Structure. The molecular packing modes of BDPA–Bz and BDPA–Ac are very similar to each other, and the benzene and acetone guest are also located on the same sites. Only the crystal structure of BDPA–Bz is, accordingly, shown in Fig. 2.

The numbers of interatomic contacts less than 4.0 Å between the radical and guest molecule are 7 and 6 in BDPA–Bz and BDPA–Ac, respectively. The shortest contacts in BDPA–Bz and BDPA–Ac are 3.376(6) and 3.67(2) Å, respectively. The C(12)···C(benzene) contact of 3.376(6) Å in BDPA–Bz is noticeably short for the interaromatic distance. The contacts between the radical and the acetone in BDPA–Ac are unexceptional. The coordinates for the center of gravity of the benzene guest are (0.78, 0.02, 0.40), which correspond to that of the carbonyl carbon atom (0.807, 0.029, 0.416) of the acetone guest. Since these positions are near to the center of inversion (1, 0, 1/2), the benzene and acetone guests form respective molecular pairs at the centers of the inversion of the (0, 0, 1/2) and (1/2, 1/2, 0) types. The shortest contacts within the pairs are 3.623(7) Å for C(benzene)···C(benzene) and 3.69(3) Å for O(acetone)···C(acetone). These facts suggest that the inclusion of benzene and acetone is attributed to the suitable size of the guest for the cavity formed by the radical molecules with a propellor shape, but not to

Table 6. Pertinent Intermolecular Contacts (l) in BDPA–Bz Crystal[a] and Sum of Triple Products in Eq. 3

Atom	Atom	ADC[b]	l/Å	Atom	Atom	ADC	l/Å
Along a axis (translation)							
C(13)	C(16)	65501	3.943	C(13)	C(21)	65501	3.789
C(14)	C(16)	65501	3.620	C(14)	C(17)	65501	3.884
C(14)	C(21)	65501	3.961	C(14)	C(22)	65501	3.791
C(15)	C(33)	65501	3.822				
Sum of triple products, J_{11}=6.85, 13.8, 15.6[c]							
Along (a+b) vector (screw diad)							
C(7)	C(13)	65502	3.950	C(8)	C(12)	65502	3.979
C(8)	C(22)	65502	3.960	C(8)	C(27)	65502	3.910
C(9)	C(16)	65502	3.777	C(9)	C(22)	65502	3.665
C(9)	C(27)	65502	3.934	C(15)	C(19)	65502	3.823
C(15)	C(20)	65502	3.736				
Sum of triple products, J_{12}=5.64, 7.97, 12.9							
Along (−a+b) vector (screw diad)							
C(2)	C(20)	55502	3.944	C(6)	C(20)	55502	3.951
C(6)	C(21)	55502	3.787	C(24)	C(19)	55502	3.797
C(24)	C(20)	55502	3.771	C(33)	C(20)	55502	3.918
C(33)	C(21)	55502	3.969				
Sum of triple products, J_{13}=3.53, 20.1, 19.8							
Along c axis in bc−plane view (diagonal glide plane)							
C(13)	C(30)	55404	3.903	C(13)	C(31)	55404	3.762
C(14)	C(30)	55404	3.980	C(25)	C(31)	55404	3.712
C(25)	C(32)	55404	3.839	C(26)	C(32)	55404	3.931
Sum of triple products, J_{14}=+0.170, −0.387, −0.385							
Along bc diagonal in bc−plane view (inversion monoad)							
C(7)	C(31)	66603	3.835	C(8)	C(31)	66603	3.921
C(31)	C(7)	66603	3.835	C(31)	C(8)	66603	3.921
Sum of triple products, J_{15}=−0.403, −0.354, −0.727							

a) Estimated standard deviations are 0.005—0.01 Å. b) ADC which specifies the position of an atom in a crystal has 5-digit number consisting of three 1-digit numbers and one 2-digit number: Ta(1st digit)+Tb(2nd digit)+Tc(3rd digit)+Sn (4th and 5th digit). Ta, Tb, and Tc are the crystal lattice translation digits along the cell edges a, b, and c, respectively. A translation digit of 5 indicates the orginal cell. If Ta=4, this indicates a translation of one unit cell length along the a axis in the negative direction. Sn or symmetry operator number refers the number of the symmetry operator used to generate the coordinates of the target atom. A list of the symmetry operators relevant to the present structures are given below. (1) x, y, z (2) $1/2-x$, $1/2+y$, $1/2-z$ (3) $-x$, $-y$, $-z$ (4) $1/2+x$, $1/2-y$, $1/2+z$ c) The values are obtained for the limitation $d \leq 4.000$, 4.500, and 5.000 Å, respectively, where d is the interatomic distance used in the calculation for the sum of the triple products in Eq. 3. The unit of the value is 10^{-5}.

a particular interaction between a radical and a guest molecule.

Around the other centers of inversion, such as the (0, 0, 0) and (1/2, 1/2, 1/2) type, the pairing appears between the phenyl and fluorenyl blade and between fluorenyl blades, as shown in Fig. 2(bottom). The relevant short contacts in BDPA–Bz are 3.835(6) and 4.576(5) Å for C(7)···C(31) and C(6)···C(7), respectively; for BDPA–Ac they are 3.82(1) and 4.41(2) Å for C(19)···C(31) and C(19)···C(19), respectively. It is noticeable that C(31)–H(C31) may be one of the key groups for BDPA being crystallized into a centric space group of $P2_1/n$ with benzene or an acetone guest. Substitution of H(C31) with a chlorine atom (p-Cl–BDPA) provides a similar molecular structure to that of BDPA, but results in an acentric crystal structure with no guest molecule.[17)]

Since the dihedral angle between two fluorenyl blade amounts to 55°—58°, a unique direction for the stacking is hardly expected. Actually, the short intermolecular contacts diverge in various directions. Thus, we cannot guess the magnetic chain corresponding to the quasi-one-dimensional antiferromagnetic properties,[3,4)] despite viewing the molecular packing from various directions.

In order to speculate about the pathways of the magnetic interaction, we tried a similar method used in a discussion of the magnetic properties of 2,4,6-triphenylverdazyl radical crystal[19)] based on the McConnell's spin density Hamiltonian:[20)]

Table 7. Pertinent Intermolecular Contacts (l) in BDPA-Ac Crystal[a) and Sum of Triple Products in Eq. 3

Atom	Atom	ADC[b)	l/Å	Atom	Atom	ADC	l/Å
Along a axis (translation)							
C(25)	C(9)	65501	3.96	C(26)	C(4)	65501	3.79
C(27)	C(29)	65501	3.84				
Sum of triple products, J_{11}=3.77, 8.97, 10.3[c)							
Along (a+b) vector (screw diad)							
C(19)	C(25)	65502	3.83	C(20)	C(15)	65502	3.99
C(20)	C(24)	65502	3.85	C(20)	C(25)	65502	3.85
C(21)	C(4)	65502	3.87	C(21)	C(10)	65502	3.70
C(21)	C(15)	65502	3.96	C(27)	C(7)	65502	3.98
C(27)	C(8)	65502	3.77	C(27)	C(9)	65502	4.00
Sum of triple products, J_{12}=3.37, 8.76, 13.3							
Along (−a+b) vector (screw diad)							
C(2)	C(8)	55502	3.99	C(12)	C(7)	55502	3.79
C(12)	C(8)	55502	3.67	C(18)	C(9)	55502	3.79
C(29)	C(8)	55502	3.95	C(29)	C(9)	55502	3.94
Sum of triple products, J_{13}=1.39, 19.3, 19.4							
Along c axis in bc−plane view (diagonal glide plane)							
C(13)	C(30)	55404	3.80	C(13)	C(31)	55404	3.74
C(25)	C(31)	55404	3.75	C(25)	C(32)	55404	3.92
C(26)	C(32)	55404	3.82				
Sum of triple products, J_{14}=+0.163, −0.445, −0.469							
Along bc diagonal in bc−plane view (inversion monoad)							
C(19)	C(31)	66603	3.82	C(20)	C(30)	66603	3.97
C(20)	C(31)	66603	3.85	C(30)	C(20)	66603	3.97
C(31)	C(19)	66603	3.82	C(31)	C(20)	66603	3.85
Sum of triple products, J_{15}=−0.469, −0.957, −0.405							

a) Estimated standard deviations are 0.01—0.03 Å. b) and c) For these, refer to the same reference mark in Table 6.

$$\mathscr{H}^{\mathrm{AB}} = -\boldsymbol{S}^{\mathrm{A}}\cdot\boldsymbol{S}^{\mathrm{B}}\Sigma J_{ij}^{\mathrm{AB}}\rho_i^{\mathrm{A}}\rho_j^{\mathrm{B}}, \tag{3}$$

where $\boldsymbol{S}^{\mathrm{A}}$ ($\boldsymbol{S}^{\mathrm{B}}$) is the total spin on molecule A(B) and ρ_i^{A} (ρ_j^{B}) is the π-spin density on the i (j)-th atom in molecule A (B). Since the exchange integral (J_{ij}^{AB}) cannot be calculated rigorously, some assumption is inevitable. This Hamiltonian can be compared with well-known two-center exchange interaction operator,

$$\mathscr{H}^{\mathrm{AB}} = -2J^{\mathrm{AB}}\boldsymbol{S}^{\mathrm{A}}\cdot\boldsymbol{S}^{\mathrm{B}} \tag{4}$$

The exchange parameter (J^{AB}) for BDPA–Bz has been estimated as to be J^{AB}/k=−4.4 K[3,4) based on magnetic-susceptibility measurements.

We apply the summation in Eq. 3 to the molecular packing of BDPA. The relevant exchange integral (J_{ij}^{AB}) is taken to be directly proportional to the σ-overlap integral between 2p Slater orbitals[21) of the i- and j-th atom. We examine the contacts shorter than 4.0, 4.5, and 5.0 Å at which the overlap integrals are 0.44, 0.15, and 0.049 times as small as that at 3.6 Å, respectively. The overlap integral between the p-orbitals in crystal is generally divided into σ- and π-components. Within the σ-overlap approximation, the limitation of the interatomic distance may prohibit an overestimation of the overlap integral between distant p-orbitals which probably have a mutual angular arrangement. The σ-type overlap gives an antiferromagnetic exchange interaction.[19) Thus, the sign of the resulting exchange interaction between the i- and j-th atom is dependent on the sign of the spin density product of $\rho_i^{\mathrm{A}}\rho_j^{\mathrm{B}}$. The relevant interatomic contacts less than 4.0 Å are listed in Tables 6 and 7. The calculated sums of the triple products in Eq. 3 are listed in the same Tables.

Three sums of J_{11}, J_{12}, J_{13} for the respective crystals are much more intense than J_{14} and J_{15}. The former three are all antiferromagnetic coupling and lie exactly and nearly parallel to the ab-plane; the latter two point out of this plane. The most intense sum differs from J_{11}, which is calculated by using interatomic distances not greater than 4.0 Å (=d_{max}), to J_{13} as d_{max} is increased to 4.5 and 5.0 Å. A possible spin arrangement within the ab-plane is shown in Fig. 3. For d_{max}=4.0 Å, the main chains in both the crystals lie along the respective a-axes with J_{11} parameters. They are connected through the J_{12} and J_{13} antiferromagnetic pathway. However, these couplings are of cancellation (frustration) for the strong net exchange interaction between the chains in which the spins are antiferromagnetically coupled. This situation is inevitable, even if d_{max} is altered to 4.5 and 5.0 Å. An established example for a cancellation of the interaction is found in K_2NiF_4, whose two-dimensional antiferromagnetic properties have been elucidated by cancellation between the neighboring antiferromagnetic layers.[22) On the other hand, J_{14} and J_{15} are very weak

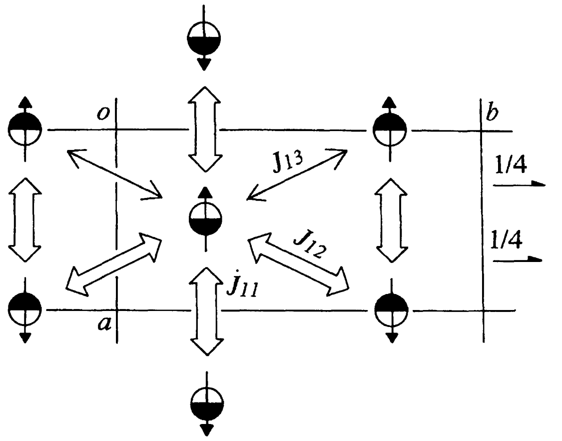


Fig. 3. One of the possible spin arrangements in the BDPA–Bz crystal. Note that the preferred direction of the spins is unspecified, but is drawn just relatively. The arrow with a figure of 1/4 shows a screw diad at $z=1/4$ (and 3/4). The position of the up or down arrow (showing the spin) nearly corresponds to that of the C(2) atom. The circle symbolizes an unspherical BDPA molecule. Refer to Tables 6 and 7 for the values of J_{ij}.

and ferromagnetic. To these may be attributed the quasi-one-dimensional antiferromagnetic susceptibilities of these crystals.

References

1) C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957).

2) W. O. Hamilton and G. E. Pake, *J. Chem. Phys.*, **39**, 2694 (1963).

3) W. Duffy, Jr., J. F. Dubach, P. A. Pianetta, J. F. Deck, D. L. Strandburg, and A. R. Miedema, *J. Chem. Phys.*, **56**, 2555 (1972).

4) J. Yamauchi, *Bull. Chem. Soc. Jpn.*, **44**, 2301 (1971); J. Yamauchi, *Phys. Lett. A*, **70A**, 238 (1979).

5) J. Yamauchi and Y. Deguchi, *Bull, Chem. Soc. Jpn.*, **50**, 2803 (1977).

6) R. Kuhn and F. A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964).

7) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351 (1968).

8) G. J. Gilmore, *J. Appl. Crystallogr.*, **17**, 42 (1984).

9) "TEXSAN--Texray Structure Analysis Package, Version 5.0," Molecular Structure Corporation, The Woodlands, TX. 77381 (1989).

10) "International Tables for X-Ray Crystallography," D. Reidel Publishing Company, Dordrecht, The Netherlands (1985), Vol. III, p.276.

11) Tables of anisotropic thermal parameters, coordinates of the hydrogen atoms, and relevant figures are deposited as Document No. 67003 at the Office of the Editor of Bull. Chem. Soc. Jpn.

12) H. O. Jenkins, *J. Am. Chem. Soc.*, **77**, 3168 (1955); P. H. H. Fischer, *Tetrahedron*, **23**, 1939 (1967); Ref. 14a.

13) a) E. Hückel, *Z. Physik.*, **70**, 204 (1931); b) A. Streitweiser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York (1961).

14) a) J. A. Pople and R. K. Nesbet, *J. Chem. Soc.*, **1954**, 571; b) The orbital coefficients appear in the following book: T. Yonezawa, T. Nagata, H. Kato, A. Imamura, and K. Morokuma, "Ryosikagaku-nyumon," Kagakudojin, Kyoto (1991).

15) a) D. E. Williams, *Acta Crystallogr., Sect. B*, **29**, 96 (1973); b) N. Azuma, Y. Deguchi, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **48**, 825 (1975).

16) K. Watanabe, J. Yamauchi, H. Ohya-Nishiguchi, Y. Deguchi, and K. Ishizu, *Bull. Inst. Chem. Res., Kyoto Univ.*, **53**, 161 (1975).

17) N. Azuma, T. Ozawa, and J. Yamauchi, Abstract No. 2244 of IUCrXVI (Beijing, Augest 1993); *J. Chem. Soc., Perkin Trans. 2*, in press.

18) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

19) N. Azuma, J. Yamauchi, K. Mukai, H. Ohya-Nishiguchi, and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **46**, 2728 (1973); N. Azuma, *Bull. Chem. Soc. Jpn.*, **55**, 1357 (1982).

20) H. M. McConnell, *J. Chem. Phys.*, **39**, 1910 (1963).

21) The program used appears in O. Kikuchi, "Bunshikidoho," Kodansya, Tokyo (1980).

22) M. E. Lines, *Phys. Rev.*, **164**, 736 (1967); R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, *Phys. Rev. Lett.*, **22**, 720 (1969); L. J. de Jongh and A. R. Miedema, *Adv. Phys.*, **23**, 1 (1974).