CONCLUSIONS

1. We have determined the group dipole moments of the $C_{Ar}-O$ bond for a series of para-substituted diphenyl ethers. We have shown that there is asymmetry in the polarity of the fragments in this series and that it is connected with asymmetry in their conformations.

2. The asymmetry in the effective conformation of the diphenyl ethers has been confirmed by means of the Kerr effect.

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STRUCTURE OF THE PRODUCT OF THE 1,3-DIPOLAR CYCLOADDITION OF C-PHENYL-N-(4-NITROPHENYL)NITRILIMINE TO 2-METHYL-4-CHLOROPHTHALAZONE HYDRAZONE

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1,3-Diarylnitrilimines react with N,N-unsubstituted hydrazones of aromatic aldehydes and ketones to form linear 1,3-addition products with the participation of the hydrazone NH_2 group (2-aryliden-4-arylhydrazidines). Products of 1,3-dipolar cycloaddition at the C=N bond were not found in these cases [1, 2].

The reaction of C-phenyl-N-(4-nitrophenyl)nitrilimine (I) with the hydrazone of 2-methyl-4-chlorophthalazone (II), in which the imine nitrogen atom of the hydrazone fragment is more basic than the amine nitrogen atom [3], gives, in addition to the expected 2-(4-nitrophenyl)-4-(2-methyl-4-chlorophthalazinylidene-1)benzhydrazidine (in tautomeric form III), an additional compound with IR, UV, and PMR spectra in accord with the structure of (2-methyl-4-chloro-1,2-dihydrophthalazine)-1-spiro-5'-[1'-(4'-nitrophenyl)-4'-amino-1',5'-dihydro-1',2',4'-triazole] (IV) which is the product of the 1,3-dipolar cycloaddition of nitrilimine (I) at the C=N bond of hydrazone (II). In contrast to expectation, product (IV) does not react with benzaldehyde or 4-nitrobenzaldehyde.

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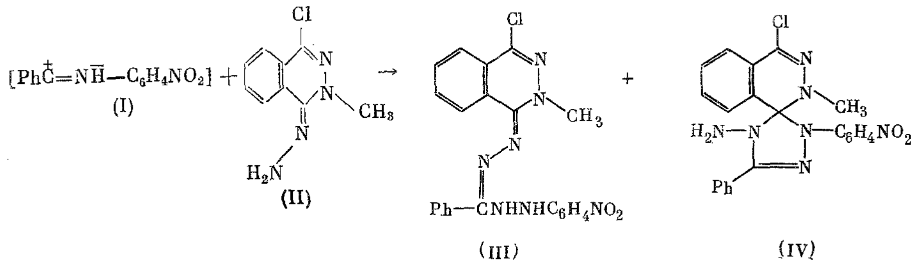
TABLE 1. Non-Hydrogen Atom Coordinates ($\cdot 10^4$)

Atom	X	Y	Z	Atom	X	Y	Z
Cl	3050(1)	4631(1)	−14(1)	C^7	1484(2)	4170(2)	2554(2)
N^1	1367(2)	5390(2)	732(2)	C^8	564(2)	4941(2)	2406(2)
N^2	580(2)	5476(2)	1411(2)	C^9	−130(3)	6349(3)	1224(4)
N^3	−542(2)	4481(2)	2436(2)	C^{10}	−1143(2)	5034(2)	3089(2)
N^4	−966(2)	3787(2)	1681(3)	C^{11}	1406(2)	6170(2)	3797(2)
N^5	543(2)	5599(2)	3320(2)	C^{12}	1305(2)	6649(2)	4761(2)
N^6	−534(2)	5685(2)	3640(2)	C^{13}	2184(3)	7189(2)	5279(3)
N^7	4103(2)	7810(2)	5389(2)	C^{14}	3168(2)	7276(2)	4827(3)
O^1	4974(2)	7880(2)	4979(2)	C^{15}	3274(2)	6837(2)	3850(3)
O^2	4010(2)	8171(2)	6267(2)	C^{16}	2406(2)	6293(2)	3339(3)
C^1	2105(2)	4701(2)	906(2)	C^{17}	−2354(2)	4934(2)	3169(2)
C^2	2209(2)	4023(2)	1785(2)	C^{18}	−2791(3)	5531(3)	3906(3)
C^3	3014(3)	3261(2)	1940(3)	C^{19}	−3922(3)	5486(3)	4024(4)
C^4	3113(3)	2691(2)	2845(3)	C^{20}	−4626(3)	4861(3)	3399(3)
C^5	2426(3)	2870(2)	3621(3)	C^{21}	−4194(3)	4269(3)	2662(4)
C^6	1605(3)	3595(2)	3466(3)	C^{22}	−3065(3)	4302(3)	2550(3)

TABLE 2. Hydrogen Atom Coordinates ($\cdot 10^3$)

Atom	X	Y	Z	Atom	X	Y	Z
H^3	351(3)	318(3)	143(3)	H^{15}	404(3)	695(3)	352(3)
H^4	373(3)	225(3)	297(3)	H^{16}	244(3)	599(2)	265(2)
H^5	253(3)	247(2)	426(3)	H^{18}	−231(3)	598(3)	437(3)
H^6	110(3)	375(3)	400(3)	H^{19}	−416(3)	586(4)	459(3)
$H^{9,1}$	25(4)	696(3)	166(3)	H^{20}	−545(3)	481(3)	344(3)
$H^{9,2}$	−26(3)	648(3)	48(3)	H^{21}	−471(3)	383(3)	216(3)
$H^{9,3}$	−87(4)	613(3)	142(3)	H^{22}	−279(3)	392(3)	202(3)
H^{12}	57(3)	658(2)	504(2)	$H^{N4,1}$	−104(3)	406(3)	100(3)
H^{13}	221(3)	748(2)	601(3)	$H^{N4,2}$	−50(3)	326(3)	184(3)



An x-ray diffraction structural study was carried out to determine the actual structure of product (IV).

EXPERIMENTAL

Hydrazidine (III) and Spiro Product (IV). A sample of 1.4 g (5 mmoles) benzoyl chloride 4-nitrophenylhydrazone was added to a solution of 1 g (5 mmoles) 2-methyl-4-chlorophthalazone hydrazone and 0.7 ml $(C_2H_5)_3N$ in 40-50 ml dry benzene. The mixture was stirred for 4 h and left to stand overnight. The precipitate was filtered off and washed repeatedly with water and ethanol. Drying yielded 1.2 g (60%) analytically pure hydrazidine (III) as a yellow powder which decomposes upon heating above 165°C. UV spectrum (λ_{max}, nm (log ε)) in dioxane: 383 (4.33), 295 (4.06). PMR spectrum (δ, ppm, in DMSO-d_6): 9.51 (1H, H^8), 9.17 s (1H, N=CNH), 8.58 s (1H, NHAr), 8.08 d and 6.87 d (4H, AA'BB', $C_6H_4NO_2$, J = 9 Hz), 7.63 m (5H, Ph and H^5–H^7), 3.70 s (3H, NCH_3). Found: C, 58.51; H, 4.20; N, 21.38%. Calculated for $C_{22}H_{18}ClN_7O_2$: C, 58.99; H, 4.02; N, 21.90%.

The mother liquor was evaporated to dryness and the residue was subjected to chromatography on a column loaded with μ40/160 silica gel using 2:1 petroleum ether–diethyl ether eluent to yield 0.3 g (14%) spiro product (IV) with mp 177-178°C (from 1:1 ethanol–ether). UV spectrum (λ_{max}, nm (log ε)) in dioxane: 410 (4.30), 322 (4.06), 250 (4.30); in CH_3OH: 420, 316, 248. IR spectrum (ν, cm^{-1}, in Vaseline): 3334, 3205 (NH_2). PMR spectrum (δ, ppm, in $CDCl_3$): 2.97 s (3H, NCH_3), 3.42 s (2H, NH_2), 6.88 d and 7.98 d (4H, AA'BB', $C_6H_4NO_2$), 7.50 m (3H, H^5–H^7), 8.02 m (1H, H^8). Found: C, 58.95; H, 4.10; Cl, 8.21; N, 21.79%. Calculated for $C_{22}H_{18}ClN_7O_2$: C, 58.99; H, 4.02; Cl, 7.93; N, 21.90%. At 20°C, the monoclinic crystals of (IV) have a = 12.034(3), b = 13.437(4), c = 12.682(3) Å, β = 97.39(2)°, d_{calc} = 1.46 g/cm³, Z = 4, space group $P2_1/c$.

TABLE 3. Interatomic Distances

Bond	d, Å	Bond	d, Å
C^1-C^2	1,434(4)	$C^{22}-C^{17}$	1,378(5)
C^2-C^3	1,405(4)	C^1-Cl	1,733(3)
C^2-C^7	1,404(4)	N^2-C^9	1,452(4)
C^3-C^4	1,372(5)	N^3-N^4	1,387(4)
C^4-C^5	1,385(5)	N^5-C^{11}	1,368(4)
C^5-C^6	1,384(5)	$C^{10}-C^{17}$	1,480(4)
C^6-C^7	1,382(5)	$C^{14}-N^7$	1,443(4)
C^7-C^8	1,510(4)	N^7-O^1	1,233(4)
C^8-N^2	1,454(4)	N^7-O^2	1,232(4)
N^2-N^1	1,366(4)	C^3-H^3	0,95(4)
N^1-C^1	1,282(4)	C^4-H^4	0,95(4)
C^8-N^3	1,472(4)	C^5-H^5	0,96(3)
N^3-C^{10}	1,384(4)	C^6-H^6	0,99(4)
$C^{10}-N^6$	1,288(4)	$C^9-H^{9,1}$	1,06(5)
N^6-N^5	1,412(3)	$C^9-H^{9,2}$	0,95(4)
N^5-C^8	1,460(4)	$C^9-H^{9,3}$	1,00(4)
$C^{11}-C^{12}$	1,401(4)	$N^4-H^{N4,1}$	0,93(4)
$C^{12}-C^{13}$	1,378(4)	$N^4-H^{N4,2}$	0,91(4)
$C^{13}-C^{14}$	1,386(4)	$C^{12}-H^{12}$	1,00(3)
$C^{14}-C^{15}$	1,392(4)	$C^{13}-H^{13}$	1,00(3)
$C^{15}-C^{16}$	1,368(4)	$C^{15}-H^{15}$	1,07(3)
$C^{16}-C^{11}$	1,411(4)	$C^{16}-H^{16}$	0,97(3)
$C^{17}-C^{18}$	1,385(5)	$C^{18}-H^{18}$	0,97(3)
$C^{18}-C^{19}$	1,390(5)	$C^{19}-H^{19}$	0,95(4)
$C^{19}-C^{20}$	1,371(6)	$C^{20}-H^{20}$	1,00(4)
$C^{20}-C^{21}$	1,379(6)	$C^{21}-H^{21}$	1,01(4)
$C^{21}-C^{22}$	1,385(5)	$C^{22}-H^{22}$	0,94(4)

The unit cell parameters and intensities of 2571 reflections with $F^2 > 3\sigma$ were measured on an automatic four-circle Hilger–Watts diffractometer with $\lambda\, Cu\, K_\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scanning, and $\theta \leq 66°$.

The structure was found by the direct method using the MULTAN program and refined by the method of least squares, initially in the isotropic approximation and then in the anisotropic approximation. All the hydrogen atoms were located in the difference map and refined isotropically in the final stage. The final divergence factors were $R = 0.054$ and $R_W = 0.064$. All the calculations were carried out on an Eclipse S/200 computer using the EXTL programs modified by A. I. Yanovskii and R. G. Gerr. The coordinates of the non-hydrogen atoms are given in Table 1 and the coordinates of the hydrogen atoms are given in Table 2.

RESULTS AND DISCUSSION

Figure 1 gives a general view of the molecule studied (the bond lengths are given in Table 3 and the bond angles are given in Table 4) and indicates that this compound is the spiro product (IV). It consists of a phthalazine fragment $[N^1N^2C^1-C^8]$ having a spiro fusion at C^8 with a 1,2,4-triazoline ring $[N^3C^{10}N^5N^6C^8]$ which is connected to an NH_2 group, phenyl ring, and nitrophenyl ring.

The phthalazine ring is planar (P1) to within ±0.061 Å (Table 5). Separately, the pyridazine ring (P2) and the fused benzene ring (C^2-C^7, P3) are more planar (to ±0.050 and ±0.017 Å, respectively). The P1/P2 angle is 1.9°. The P1/P3 angle is 2.1°, while the P2/P8 angle is 4.0°. The flexure of the phthalazine system in spiro product (IV) is the same as in 1-dimethylamino-4-chlorophthalazine [4]. The best mean-square plane (P4) in the pyridazine ring includes only the $N^1C^1C^2C^7$ atoms and, on the whole, has a distorted boat conformation. The N^2 atom especially extrudes from the P4 plane (by 0.1294 Å).

The involvement of the C^8 atom in the spiro fusion leads to its conversion to the sp^3 state and, as a result, to an increase in the C^7-C^8 and N^2-C^8 bond distances to values typical for single bonds. In comparison with phthalazine, the $N^1N^2C^8$ bond angle is expanded to 126.4°, the $C^2C^7C^8$ bond angle is expanded to 121.4°, while $N^2C^8C^7$ bond angles is reduced to 110.9°. These angles in phthalazine are 118.5°, 115.3°, and 126.1°, respectively [5], i.e., the nature of the change of the bond angles in the phthalazine fragment of the spiro product (IV) is the same as in phthalazone hydrazone salts [3, 6] protonated at N^2 of the ring or in triazolino[3,4-a]phthalazinium salts [7] and is the consequence of the change in the electronic state of the C^8 and N^2 atoms and not of the bulkiness of the fragment fused to the spiro system.

The triazoline ring is an indistinct envelope with a flexure at $N^5 \ldots N^3$. The C^8 atom extrudes from the P5 plane $[N^5N^6C^{10}N^3$ atoms] by 0.232 Å (the torsional angles are given in Table 6). The atoms directly bound to the triazoline ring also extrude from the P5 plane (see Table 5).

The planes of the phthalazine and triazoline rings are virtually perpendicular (the P1/P5 angle is 89.9° and the P2/P5 angle is 89.1°). The rotation of the 4-nitrophenyl ring [P6, $C^{11}-C^{16}$] about the $C^{11}-N^5$ bond cal-

TABLE 4. Bond Angles ω

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$N^2N^1C^1$	118,3(2)	$C^3C^2C^7$	119,0(3)	$C^{12}C^{11}C^{16}$	118,7(3)
$N^1N^2C^8$	126,4(2)	$C^2C^3C^4$	120,4(3)	$C^{11}C^{12}C^{13}$	120,7(3)
$N^1N^2C^9$	114,0(3)	$C^3C^4C^5$	120,2(3)	$C^{12}C^{13}C^{14}$	119,4(3)
$C^8N^2C^9$	117,9(3)	$C^4C^5C^6$	120,1(3)	$N^7C^{14}C^{13}$	119,4(3)
$N^4N^3C^8$	121,2(2)	$C^5C^6C^7$	120,6(3)	$N^7C^{14}C^{15}$	119,8(3)
$N^4N^3C^{10}$	126,9(2)	$C^2C^7C^6$	119,7(3)	$C^{13}C^{14}C^{15}$	120,9(3)
$C^8N^3C^{10}$	109,5(2)	$C^2C^7C^8$	121,4(2)	$C^{14}C^{15}C^{16}$	119,8(3)
$N^6N^5C^8$	112,8(2)	$C^6C^7C^8$	118,9(3)	$C^{11}C^{16}C^{15}$	120,4(3)
$N^6N^5C^{11}$	120,0(2)	$N^2C^8N^3$	110,0(2)	$C^{10}C^{17}C^{18}$	117,1(3)
$C^8N^5C^{11}$	126,9(2)	$N^2C^8N^5$	113,1(2)	$C^{10}C^{17}C^{22}$	124,2(3)
$N^5N^6C^{10}$	105,6(2)	$N^2C^8C^7$	110,9(2)	$C^{18}C^{17}C^{22}$	118,7(3)
$O^1N^7O^2$	122,2(3)	$N^3C^8N^5$	97,2(2)	$C^{17}C^{18}C^{19}$	120,6(3)
$O^1N^7C^{14}$	118,7(3)	$N^3C^8C^7$	111,1(2)	$C^{18}C^{19}C^{20}$	120,3(4)
$O^2N^7C^{14}$	119,1(3)	$N^5C^8C^7$	113,8(2)	$C^{19}C^{20}C^{21}$	119,1(4)
ClC^1N^1	115,0(2)	$N^3C^{10}N^6$	112,5(2)	$C^{20}C^{21}C^{22}$	120,8(4)
ClC^1C^2	119,3(2)	$N^3C^{10}C^{17}$	126,0(2)	$C^{17}C^{22}C^{21}$	120,4(3)
$N^1C^1C^2$	125,6(3)	$N^6C^{10}C^{17}$	121,5(3)	$H^{N4,1}N^4H^{N4,2}$	120(3)
$C^1C^2C^3$	124,1(3)	$N^5C^{11}C^{12}$	119,8(3)	$H^{N4,1}N^4N^3$	111(2)
$C^1C^2C^7$	116,8(3)	$N^5C^{11}C^{16}$	121,5(3)	$H^{N4,2}N^4N^3$	102(2)

TABLE 5. Coefficients of the Equations AX + BY + CZ = D of the Planar Fragments of Molecule (IV) and Extrusions of Atoms from These Planes

Fragment	*A*	*B*	*C*	*D*	Atom extrusions, Å
*P*1	−0,5772	−0,6585	−0,4829	−6,033	N^1 −0,061; N^2 0,061; C^1 −0,054; C^2 0,023; C^3 0,058; C^4 0,030; C^5 −0.050; C^6 −0,041; C^7 0,002; C^8 −0,034
*P*2	−0,5555	−0,6592	−0,5069	−6,0554	N^1 −0,033; N^2 0,050; C^1 −0,011; C^2 0,040; C^7 −0,027; C^8 −0,014; Cl* −0,077; N^{3*} 1,116; N^{5*} −1,083; C^{9*} −0,150
*P*3	−0,5992	−0,6602	−0,4530	−5,9867	C^2 −0,017; C^3 0,005; C^4 0,012 C^5 −0,017; C^6 0,005; C^7 0,012
*P*4	−0,5876	−0,6347	−0,5018	−5,9652	N^1 0,0096; C^1 −0,018; C^2 0,017; C^7 −0,008; N^{2*} 0,129; C^{8*} 0,064
*P*5	−0,1496	−0,6652	−0,7715	−1,9278	N^5 0,006; N^6 −0,011; C^{10} 0,011; N^3 −0,007; C^{8*} 0,232; N^{4*} 0,125; C^{11} −0,066; C^{17*} 0,068; N^{2*} 1,599; C^7 −0,756
*P*6	0,3004	0,8224	−0,4810	4,2130	C^{11} −0,018; C^{12} 0,014; C^{13} 0,001; C^{14} −0,011
*P*7	−0,0981	0,7205	−0,6865	2,3697	C^{17} 0,000; C^{18} 0,004; C^{19} −0,006; C^{20} 0,002; C^{21} 0,002; C^{22} −0,004
*P*8	−0,2817	0,8505	−0,4441	4,7685	O^1 −0,001; O^2 −0,001; N^7 0,004; C^{14} −0,001

*These atoms not included in calculating the equations for the planes.

culated from the torsional angles (see Table 6) is −13°,* while the dihedral angle between planes P5 and P6 is 19.2°. The rotation of the phenyl ring [P7, $C^{17}-C^{22}$] about the $C^{17}-C^{10}$ bond is 4°* (calculated from the torsional angles given in Table 6), while the P5/P7 and P6/P7 angles are 5.1° and 17.7°, respectively. The NO_2 group [plane P8, $O^1O^2N^7C^{14}$] is virtually coplanar with the $C^{11}-C^{16}$ ring (the P6/P8 angle is 2.9° and the angle φ about the N^7-C^{14} bond is 2°).

There is, of course, no unified conjugation system in spiro product (IV) though conjugation is found in the separate fragments. Thus, the bond lengths in the chlorobenzylidenehydrazine fragment [$ClN^1N^2C^1-C^7$] in the phthalazine system are the same as in the corresponding fragment of the phenylhydrazone of benzoyl chloride [8]. The long-wavelength band in the UV spectrum of the spiro product is analogous to that in the UV spectrum of the 4-nitrophenyl hydrazone of benzamide [$4-O_2NC_6H_4-NHN{=}C(NH_2)Ph$, λ_{max} 435 in ethanol], whose framework is the basis of the triazoline ring with attached benzene rings.

The existence of conjugation in the triazoline ring is also indicated by the bond lengths. In the hydrazone fragment $C^{11}-N^5-N^6-C^{10}$, these bond lengths are virtually the same as in the 4-nitrophenylhydrazone of benzoyl chloride [9], from which nitrilimine (I) is generated. The N^3-C^{10} bond length (1.384 Å) is shorter than the value in the standard. In addition, in the absence of conjugation, the rotations of the phenyl and ni-

TABLE 6. Torsional Angles τ

Angle	τ, deg	Angle	τ, deg
$C^8N^3C^{10}N^6$	−11,5(3)	$C^{18}C^{17}C^{10}N^6$	−3,6(4)
$N^3C^{10}N^6N^5$	2,2(3)	$C^{18}C^{17}C^{10}N^3$	177,3(5)
$C^{10}N^6N^5C^8$	8,2(3)	$C^{22}C^{17}C^{10}N^6$	175,4(5)
$N^6N^5C^8N^3$	−13,7(3)	$C^{22}C^{17}C^{10}N^3$	−3,7(4)
$N^5C^8N^3C^{10}$	14,4(3)	$C^{10}N^3N^4H^{N4,1}$	100(4)
$C^{12}C^{11}N^5N^6$	15,7(3)	$C^{10}N^3N^4H^{N4,2}$	−131(4)
$C^{12}C^{11}N^5C^8$	−170,6(4)	$C^8N^3N^4H^{N4,1}$	60(4)
$C^{16}C^{11}N^5N^6$	−164,1(4)	$C^8N^3N^4H^{N4,2}$	68(4)
$C^{16}C^{11}N^5C^8$	9,6(3)		

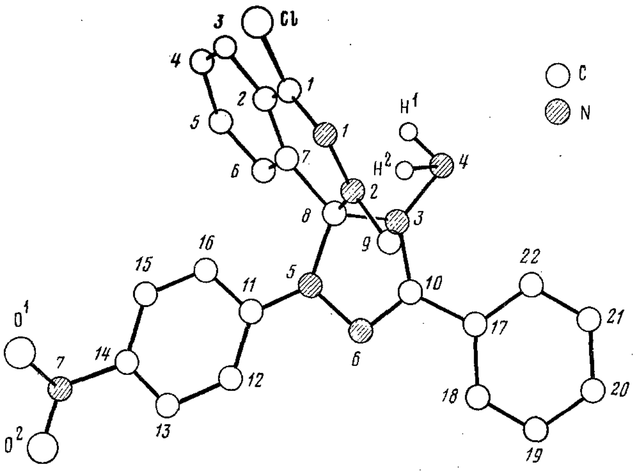


Fig. 1. General view of the spiro product (IV).

trophenyl rings about the $C^{11}-N^5$ and $C^{17}-C^{10}$ bonds should be greater since the $C^{16} \ldots C^8$ contact [2.989(4) Å] and $C^{22} \ldots N^3$ contact [3.067(5) Å] are less than the sum of the Van der Waals radii.

The N^3-N^4 bond length is closer to similar bonds in the sodium salt of 3-mercapto-4-amino-1,2,4-triazole (1.414 Å [10] and in the hydrobromide salt of 3,4,5-triamino-1,2,4-triazole (1.383 Å [11]) than to those in hydrazine (1.453 Å [12]) or phenylhydrazine (1.46 Å [13]). The N^4 atom has pyramidal conformation (the sum of the angles is 333° and C_p^N 0.68 [4]). Analysis of the Newman projection down the N^3-N^4 bond relative to the torsional angles angle between the directions of the unshared electron pair orbitals of atoms N^3 and N^4 is 74°, i.e., somewhat less than in hydrazine ($\sim$90° [12]).

In examining the interatomic distances between non-valence-bonded atoms, we note that the $C^{22} \ldots N^4$ contact [2.964(4) Å] and $H^{22} \ldots N^4$ contact [2.30(4) Å] are less than the sums of the Van der Waals radii (1.71 Å for C, 1.50 Å for N, and 1.16 Å for H [14]) and satisfy the crystallographic criterion for a CH...N hydrogen bond ($r \leq \Sigma R_W - 0.1$ Å) [15]. The $N^2 \ldots N^4$ contact (2.982 Å) and $N^2 \ldots H^{N4,1}$ contact (2.726 Å) may also be interpreted in accord with Pimentel [15] [$R_W(N) = 1.65$ Å] as corresponding to an intramolecular NH...N hydrogen bond, but only as a rather weak example.

Intermolecular contacts less than sums of Van der Waals radii were not found. This is very unexpected for compounds having NH_2 and NO_2 groups. The shortest of the intermolecular contacts are $N^1 \ldots N^{4'}$ [$-X, 1-Y, Z$, 3.231(4) Å] and $N^1 \ldots H^{N4,1}$ (2.30(4) Å); these contacts are comparable to the N...N contact (3.23 Å) in phenylhydrazine crystals [13].

CONCLUSIONS

1. An x-ray diffraction structural analysis was carried out for the product of the 1,3-dipolar cycloaddition of C-phenyl-N-(4-nitrophenyl)nitrilimine at the C=N bond of the hydrazone of 2-methyl-4-chlorophthazone. proceeds in two directions: 1) involving the NH_2 group and 2) involving the C=N bond.

The reaction of the hydrazone of 2-methyl-4-chlorophthalazone proceeds in two directions: 1) involving the NH_2 group and 2) involving the C = N bond.

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*The signs of the rotational angles about a given bond are derived from the condition that the fragment with the atom indicated first is rotated relative to the fragment indicated second which is arbitrarily taken as stationary.

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SYNTHESIS AND MOLECULAR STRUCTURE OF 2,2,6,9-TETRAMETHYL-4,11-DIPHENYL-4,5,10,11-TETRAAZA-1,3-DIPHOSPHATRICYCLO[6.3.0.$0^{3,7}$] UNDECA-5,9-DIENE

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We were the first to demonstrate the possibility of cycloaddition at the dicoordinated phosphorus P=C bond and obtained a new class of compounds, namely, bicyclic phosphiranes, by the reaction of 2-phenyl- and 2-acetyl-5-methyl-1,2,3-diazaphosphole with diphenyldiazomethane [1].

The reaction of diazopropane on diazaphospholes apparently also gave the analogous bicyclic compounds. However, the reaction of diazapropane with 2-phenyl-5-methyl-1,2,3-diazaphospholes proceeds in a much more complex manner with the formation of a whole series of products.

In the present work, we found the structure of one of the products of this reaction. The x-ray diffraction structural study showed that this product is 2,2,6,9-tetramethyl-4,11-diphenyl-4,5,10,11-tetraaza-1,3-diphosphatricyclo[6.3.0.$0^{3,7}$]deca-5,9-diene (I).

EXPERIMENTAL

A sample of 11.5 g 2-phenyl-5-methyl-1,2,3-diazaphosphole was added to a solution of an excess of diazopropane in abs. ether at −60°C. Nitrogen liberation was noted and the color of the reaction mixture changed from pink to yellow. A precipitate was formed. The reaction mixture was maintained for 1.5 h at from −60 to −40°C and then the temperature was raised to about 25°C. The precipitate was removed by filtration to yield 5.5 g (I) with mp 260°C as colorless prisms (from EtOH and MeCN), δ^{31}P 62 ppm. Found: C, 64.01; H, 6.11; N, 14.21; P, 15.29%. Calculated for $C_{21}H_{24}N_4P_2$: C, 63.94; H, 6.13; N, 14.21; P, 15.72%. IR spectrum (ν, cm^{-1}): 520, 640, 753, 235, 1315, 1490, 1585. PMR spectrum ($CHCl_3$, δ, ppm): 0.95 m (3H), 2.17 s (3H), 3.9 m (1H).

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