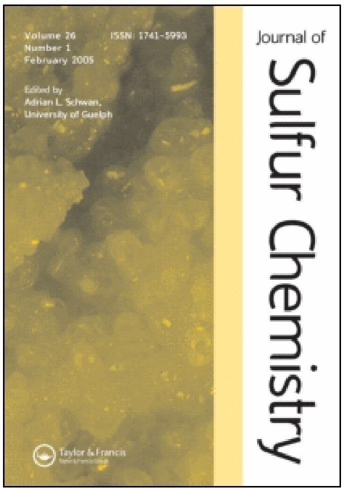

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NMR study and AIM analysis for the ylide rotamers from the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 2-mercapto-1-methylimidazole

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Stable crystalline phosphorus ylides are obtained in excellent yields from the 1:1:1 addition reactions between triphenylphosphine and dialkyl acetylenedicarboxylates, in the presence of an SH-heterocyclic compound, such as 2-mercapto-1-methyl imidazole. These stable ylides exist in solution as a mixture of the two geometrical isomers as a result of restricted rotation around the carbon–carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. In the recent work, an NMR study and the stability of the Z- and E-isomers were undertaken for the two rotamers of phosphorus ylides involving 2-mercapto-1-methylimidazole by natural population analysis.

Keywords: stable phosphorus ylides; dialkyl acetylenedicarboxylates; rotamer; AIM, SH-heterocyclic compounds

1. Introduction

Ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products and compounds with biological and pharmacological activity (*1*). The synthesis of phosphorus ylides is an important reaction in organic chemistry because of the application of these compounds in the synthesis of organic products (*2–30*). Phosphorus ylides are most often prepared by treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from the reaction of phosphine and an alkyl halide (*4–8*), though they can be obtained by the Michael addition of phosphorus nucleophiles to activated olefins (*3,4*).

A facile synthesis of the reaction between triphenylphosphine **1**, dialkyl acetylendicarboxylates **2** and 2-mercapto-1-methylimidazole **3** (as an SH-heterocyclic compound) have been reported earlier (*31*) for generation of phosphorus ylides **4a** and **4c** involving two geometrical isomers, such as Z- and E-isomers. The reaction is shown in Figure 1. For assignment of the two Z- and

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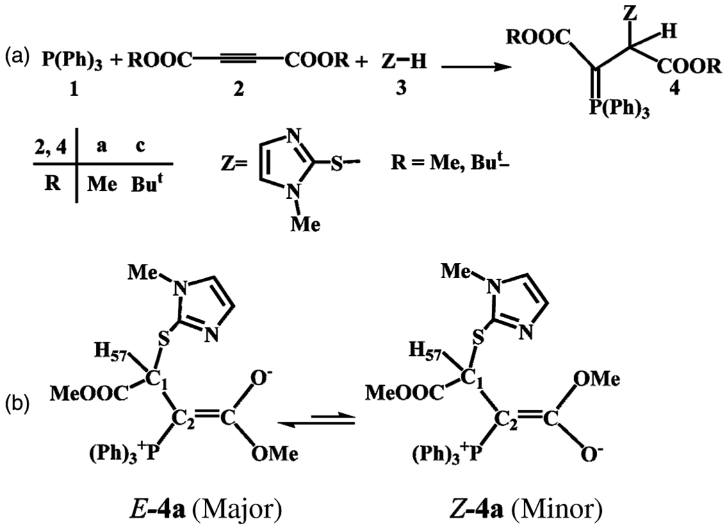

Figure 1. (a) The reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2** (**2a** or **2b**) and 2-mercapto-1-methylimidazole **3** for generation of stable phosphorus ylides **4** (**4a** or **4c**). (b) The two isomers *Z*-**4a** and *E*-**4a** (minor and major, respectively) of ylide **4a**.

E-isomers as a minor or major form in phosphorus ylides **4a** and **4c** containing a 2-mercapto-1-methylimidazole, the *Z*- and *E*-isomers were optimized for all ylide structures at the HF/6-31G(d,p) level of theory by Gaussian 98 package program (*32*). The relative stabilization energies for both the geometrical isomers have been calculated at the B3LYP/6-311++G(d,p) level. Atoms in molecules (AIM) and the calculation of charge on the atoms by natural population analysis (NPA) and the CHelpG keyword at the HF/6-31G(d,p) level of theory have been performed in order to gain a better understanding of the most geometrical parameters in both the *E*-**4a** and *E*-**4c** and the *Z*-**4a** and *Z*-**4c** of phosphorus ylides. The numbers of critical points and intramolecular hydrogen bonds as well as the charge of atoms that were constructed on the *Z*- and *E*-isomers have been recognized. The results altogether reveal the effective factors on stability of *Z*- and *E*-ylide isomers. In addition, J_{x-y}, the values of proton and carbon coupling constants, and also chemical shifts (δ^{H}_{iso}, δ^{C}_{iso}) have been calculated at the mentioned level using the SPINSPIN keyword.

2. Results and discussion

2.1. *Calculations*

Recently, different reports have been published on the synthesis of stable phosphorus ylides from the reaction between triphenylphosphine and reactive acetylenic esters in the presence of N—H, C—H or S—H heterocyclic compounds. These ylides usually exist as a mixture of the two geometrical isomers, although some ylides exhibit one geometrical isomer. Assignment of the stability of the two *Z*- and *E*-isomers is impossible in phosphorus ylides by experimental methods such as ^{1}H and ^{13}C NMR and IR spectroscopy, mass spectrometry and elemental analysis data. For this reason, quantum mechanical calculations have been performed in order to gain a better understanding of the most important geometrical parameters and also relative energies of both the geometrical isomers.

In order to determine more stable form of both the geometrical isomers (*Z*-**4a** and *Z*-**4c** or *E*-**4a** and *E*-**4c**) of ylides (**4a** or **4c**), first their structures were optimized at the HF/6-31G(d,p) level of theory (*33*) by Gaussian 98 program package. Also relative stabilization energy of the two isomers has been calculated at the HF/6-31G(d,p) and B3LYP/6-311++G(d,p) levels (Figures 2 and 3). The relative stabilization energies for the two isomers (*Z*-**4a** and *Z*-**4c** and *E*-**4a** and *E*-**4c**) are reported in Table 1, as can be seen, the *E*-**4a** and the *E*-**4c** isomers are more stable than the *Z*-**4a** and *Z*-**4c** forms (2.97 and 1.73 kcal/mol, respectively) at the B3LYP level.

Further investigation was undertaken in order to determine more effective factors on stability of the two *Z*- and *E*-isomers, on the basis of AIM calculations (*34*) at the HF/6-31G(d,p) level of theory by the AIM2000 program package (*35*). In recent years, AIM theory has often been applied in the analysis of H-bonds. In this theory, the topological properties of the electron

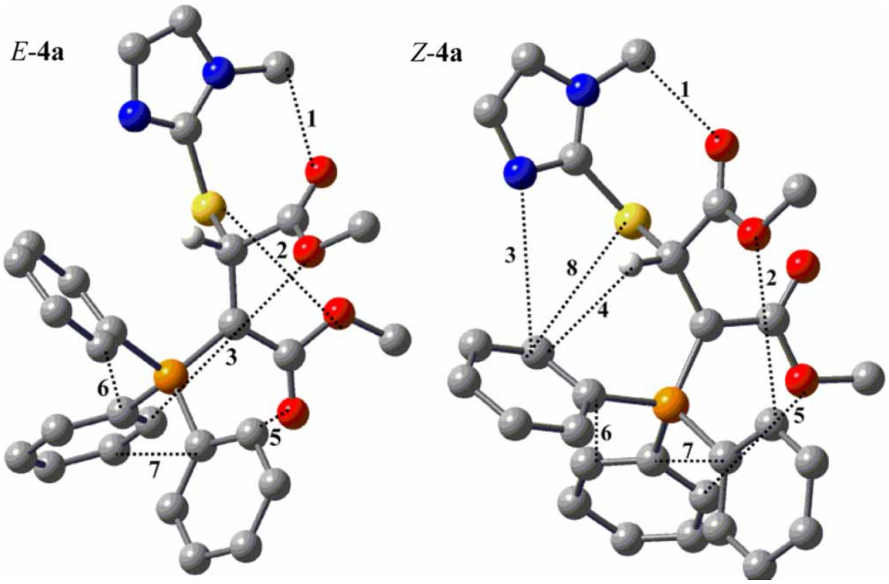

Figure 2. Intramolecular hydrogen bonds (dotted lines) in the *E*-**4a** and *Z*-**4a** geometrical isomers of the stable ylide **4a**.

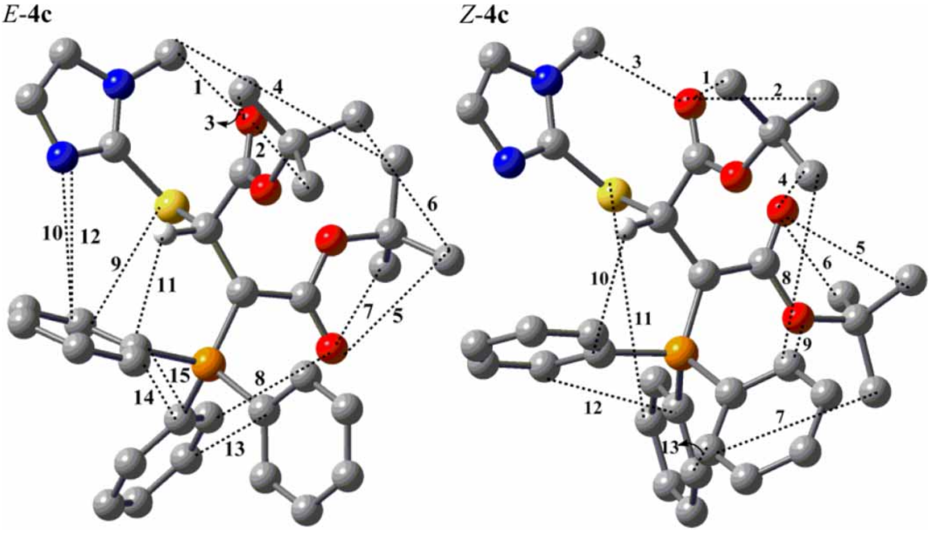

Figure 3. Intramolecular hydrogen bonds (dotted lines) in the *E*-**4c** and *Z*-**4c** geometrical isomers of the stable ylide **4c**.

Table 1. The relative energy (kcal/mol) for for the two Z- and E-isomers of ylides **4a** and **4c**, obtained at the HF/6-31G(d,p) and B3LYP/6-311++G(d,p) levels.

Conformer	HF	B3LYP
Z-**4a**	4.22	2.97
E-**4a**	0.00	0.00
Z-**4c**	2.43	1.73
E-**4c**	0.00	0.00

density distribution are derived from the gradient vector field of the electron density $\rho(r)$ and on the Laplacian of the electron density $\nabla^2\rho(r)$. The Laplacian of the electron density, $\nabla^2\rho(r)$, identifies regions of space wherein the electronic charge is locally depleted [$\nabla^2\rho(r) > 0$] or built up [$\nabla^2\rho(r) < 0$] (*34*). Two interacting atoms in a molecule form a critical point in the electron density, where $\nabla\rho(r) = 0$, called the bond critical point (BCP). The values of charge density and its Laplacian at these critical points give useful information regarding the strength of the H-bonds (*35*). The ranges of $\rho(r)$ and $\nabla^2\rho(r)$ are (0.002–0.035)e/a_0^3 and (0.024–0.139)e/a_0^5, respectively, if H-bonds exist (*36*). The AIM calculation indicates intramolecular hydrogen bonds and critical points (H-BCP) for the Z-**4a** and Z-**4b** and the E-**4a** and E-**4b** isomers. Intramolecular H-BCPs are shown in Figures 2 and 3 (dotted line). The electron densities (ρ), Laplacian of electron density $\nabla^2\rho(r)$ and energy density $-H(r)$ are also reported in Tables 2 and 3. A negative total energy density at the BCP reflects a dominance of potential energy density, which is the consequence of accumulated stabilizing electronic charge (*37*). Herein, the number of hydrogen bonds in both categories (E-**4a** and Z-**4a**) and (E-**4c** and Z-**4c**) are (7 and 8) and (15 and 13), respectively. The values of ρ and $\nabla^2\rho(r)$ are in the ranges (0.004–0.022 and 0.005–0.012)e/a_0^3, (0.002–0.013 and 0.002–0.013)e/a_0^5, (0.017–0.060 and 0.018–0.047)e/a_0^5 and (0.003–0.049 and 0.007–0.050)e/a_0^5, respectively. In addition, the Hamiltonian [-$H(r)$] is in the range (4.3–18.2 and 8.4–18.3 au) and (2.1–18.1 and 4.8–18.1 au) (Tables 2 and 3). These HBs show $\nabla^2\rho(r) > 0$ and $H(r) < 0$, which according to the classification of Rozas *et al.* (*38*) are medium-strength hydrogen bonds. In both ylides, the dipole moment for the E-**4a** and E-**4c** isomers (3.27 and 3.39 D, respectively) are smaller than the Z-**4a** and Z-**4c** isomers (6.17 and 6.19 D, respectively) and the value of $-H_{\text{tot}}$ ($= \sum H(r)$) for the two Z-**4a** and Z-**4c** isomers (101.3 and 149.6 au, respectively) are larger than the E-**4a** and E-**4c** isomers (91.5 and 144.7 au, respectively). These differences in the most important geometrical parameters of the E-**4a** and E-**4c** with respect to the Z-**4a** and Z-**4c**, involving a small difference in dipole moment and a considerable difference in $-H(r)$ and also approximately the same number of hydrogen bonds, altogether, make only the slightest stability on these isomers in comparison with the Z-**4a** and Z-**4c** forms. Moreover, the total number of hydrogen bonds in Z-**4c** and E-**4c** (13 and 15) are more than that in Z-**4a** and E-**4a** (8 and 7);

Table 2. The values of $\rho \times 10^3$, $\nabla^2\rho \times 10^3$ and Hamiltonian $-H(r) \times 10^4$ for both the Z-**4a** and the E-**4a** isomers of ylide **4a** calculated at the H-BCPs.

E	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$	Z	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$
1	4.34	76.83	8.9	1	9.74	46.65	8.5
2	21.55	17.49	4.3	2	5.84	36.87	9.2
3	5.64	24.23	11.1	3	4.67	17.81	8.4
4	13.40	59.68	16.1	4	11.11	30.70	17.4
5	14.74	48.01	17	5	12.03	40.60	12.2
6	11.03	40.78	15.9	6	11.70	23.88	18.3
7	10.96	38.27	18.2	7	10.19	35.37	15.3
				8	9.23	43.03	12

Note: All quantities are in atomic units.

Table 3. The values of $\rho \times 10^3$, $\nabla^2\rho \times 10^3$ and Hamiltonian $-H(r) \times 10^4$ for the two Z-**4c** and E-**4c** isomers of ylide **4c** calculated at the H-BCPs.

E	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$	Z	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$
1	11.96	46.62	13.5	1	12.03	46.64	13
2	12.26	47.72	13.3	2	12.49	48.92	14
3	8.93	34.06	8.5	3	8.62	33.44	9.1
4	3.21	11.68	5.7	4	2.91	12.80	7.6
5	3.70	15.88	2.1	5	12.55	47.96	12.5
6	2.30	2.79	5	6	13.13	49.92	12.1
7	1.75	8.10	4.1	7	2.72	8.80	4.8
8	12.92	5.99	12.8	8	2.03	7.32	4.9
9	12.39	48.23	7.3	9	8.68	35.68	12.8
10	4.58	49.53	8.8	10	10.74	40.52	18.1
11	3.21	44.76	5.7	11	4.84	16.68	9.6
12	11.48	15.88	16.8	12	8.79	32.80	16.3
13	2.64	11.68	6.9	13	9.75	33.88	14.8
14	9.11	40.14	16.1				
15	10.27	10.17	18.1				

Note: All quantities are in atomic units.

this leads to a large rigidity in these geometrical isomers in comparison with the Z-**4a** and E-**4a** forms. The rigidity of the two molecular structures by the very large intramolecular hydrogen bonds accompanied by more steric factor of the bulky *tert*-bulky groups (compared with dimethyl groups in both the E-**4a** and Z-**4a**; Figures 2 and 3) within the structures (E-**4c** and Z-**4c** forms) makes a good opportunity for the enhancement of the energy barrier. Hence, an interconversion process between the two isomer needs to pass through a very high restricted barrier energy, particularly in solution media; for this reason, it is possible to see only a single isomer as a lone isomer of **4c** (E-**4c**). On the contrary, the interconversion process for both the E-**4a** and Z-**4a** geometrical isomers pass through a considerably low energy barrier, which leads to a plausible observation of the E-**4a** and Z-**4a** (Figure 1(b)).

In the synthesis of ylides **4a** and **4c** (*31*), the ^{1}H, ^{13}C and ^{31}P NMR data showed a lone isomer of **4c** (E-**4c**) with the experimental abundance percentage of 100% as a major form and also a mixture of isomers E-**4a** and Z-**4a** with abundance percentage of 65% for E-**4a** as a major form.

Also, the charge on different atoms, which are calculated by the NPA and AIM methods and also the CHelpG keyword at the HF/6-31G(d,p) level, are reported in Table 4 for the two Z- and E-isomers of ylides **4a** and **4c**. There is a good agreement between the results of the three methods.

Table 4. The charges on different atoms for both Z- and E-isomers in ylides **4a** and **4c** calculated at HF/6-31G(d,p) levels.

Number of atoms	Z-**4a**	E-**4a**	Z-**4c**	E-**4c**
C1	2.69×10^{-1a}, $(0.05)^b$, $(\times 0.44)^c$	2.60×10^{-1}, (0.01), (−0.47)	2.86×10^{-1}, (0.12), (−0.43)	3.08×10^{-1}, (0.23), (−0.43)
C2	-7.72×10^{-1}, (−0.44), (−0.83)	-8.54×10^{-1}, (−0.44), (−0.84)	-7.63×10^{-1}, (−0.48), (−0.83)	-7.37×10^{-1}, (−0.51), (−0.83)
C4	1.85, (0.89), (0.91)	1.88, (0.88), (0.92)	1.88, (0.92), (0.91)	1.87, (0.96), (0.91)
O5	−1.38, (−0.65), (−0.76)	−1.42, (−0.74), (−0.79)	−1.41, (−0.66), (−0.76)	−1.42, (−0.76), (−0.76)
O6	−1.30, (−0.44), (−0.66)	−1.28, (−0.37), (−0.63)	−1.31, (−0.65), (−0.69)	−1.30, (−0.62), (−0.69)
P3	3.23, (0.26), (1.75)	3.24, (0.23), (1.75)	3.25, (0.29), (1.75)	3.24, (0.29), (1.75)

Notes: [a]Calculated by the AIM method. [b]Calculated by the CHelpG keyword. [c]Calculated by the NPA method.

On the basis of theoretical calculations (Table 1), the difference between the relative stability of the E-**4c** and Z-**4c** isomers is (1.73 kcal/mol) while it is greater in the E-**4a** and Z-**4a** (2.97 kcal/mol) in gas phase. This result (a slightly difference in stability) is completely consistent with the obtained results on the basis of AIM calculations for determination of the most geometrical parameters.

Furthermore, the individual chemical shifts have been characterized by NMR calculations at the mentioned level for the two major E-**4a** and E-**4c** and minor Z-**4a** and Z-**4c** geometrical isomers. The total spin–spin coupling constant is the sum of four components: the paramagnetic spin–orbit, diamagnetic spin–orbit, Fermi-contact and spin–dipole terms. The value of chemical shifts (δ) and coupling constants (J_{x-y}) are reported in Tables 5–8. As can be seen, there is good agreement between both the experimental (*31*) and theoretical chemical shifts (δ) and coupling constants (J_{x-y}). In the present work, molecular structures of ylides **4a** and **4c** involving three large atoms such as sulfur, phosphorus and nitrogen are huge with the large numbers of other atoms; for this reason, employment of basis set higher than B3LYP/6-311++G(d,p) is impossible for performance of more accurate calculations. This limitation causes a small difference between both the experimental and theoretical coupling constants in some functional groups.

Table 5. Selected ^{1}H NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in the E-**4a** isomer as a major form.

Groups	δ^H (ppm)	J_{PH} (Hz)
6H, 2s, 2 CO_2Me	3.48[a] (3.49)[b], 3.74 (3.57)	
1H, d, P−C−CH^{57}	5.55 (2.28)	17.2[a] (16.4)[b]
15H, m, 3C_6H_5	7.48–7.66 (7.48–7.83)	

Notes: [a]Experimental data in accord with the results reported in the literature (*31*). [b]Theoretical data.

Table 6. Selected ^{1}H NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in the Z-**4a** isomer as a minor form.

Groups	δ^H (ppm)	J_{PH} (Hz)
6H, 2s, 2 CO_2Me	3.58[a] (3.59)[b], 3.50 (3.43)	
1H, d, P−C−CH^{57}	5.48 (2.58)	18.7[a] (14.2)[b]
15H, m, 3C_6H_5	7.49–7.67 (7.49–7.94)	

Notes: [a]Experimental data in accord with the results reported in the literature (*31*). [b]Theoretical data.

Table 7. Selected ^{13}C NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in the Z-**4a** isomer as a minor form.

Groups	δ^C (ppm)	J_{PC} (Hz)
2s, 2OMe	50.22[a] (50.50)[b], 47.55 (45.28)	
d, C_{ipso}	125.61 (128.11)	93.1[a] (94.4)[b]
d, C_{ortho}	132.23 (132.78)	
d, C_{meta}	128.51 (125.53)	12.2 (8.1)
d, C_{para}	133.60 (135.77)	9.8 (11.2)
d,P=C	30.04 (43.33)	128.4 (169.6)
d,P−C−CH^{37}	60.23 (48.74)	24.7 (23.0)
d,C^7=O	170.34 (168.13)	12.7 (11.2)
d,C^4=O	171.23 (162.99)	12.1 (10.7)

Notes: [a]Experimental data in accord with the results reported in the literature (*31*). [b]Theoretical data.

Table 8. Selected ^{13}C NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in E-**4a** isomer as a major form.

Groups	δ^{C} (ppm)	J_{PC} (Hz)
2s, 2OMe	49.21[a] (47.43)[b], 52.62 (46.09)	
d, C_{ipso}	126.35 (128.21)	92.2[a] (91.6)[b]
d, C_{ortho}	132.25 (132.59)	
d, C_{meta}	128.99 (125.47)	11.8 (8.7)
d, C_{para}	133.61 (132.59)	9.8 (11.0)
d,$C^4{=}O$	171.23 (168.14)	10.8 (9.2)
d,$C^7{=}O$	170.35 (169.87)	12.7 (4.2)
d,$P{-}C{-}CH^{37}$	60.40 (45.69)	18.5 (10.4)
d,$P{=}C$	43.35 (31.53)	128.2 (175.1)

Notes: [a]Experimental data in accord with the results reported in the literature (*31*). [b]Theoretical data.

3. Conclusion

The assignment of the Z- and E-isomers as a major or minor form in both the ylides **4a** and **4c** were undertaken by the AIM and NPA methods and also the CHelpG keyword. Quantum mechanical calculation clarified how the ylides **4a** and **4c** exist in solution as a mixture of the two geometrical isomers. This result was in good agreement with the experimental data. In addition, the NMR study on the basis of theoretical calculations was employed for the determination of chemical shifts and coupling constants of the two major E-**4a** and E-**4c** and minor Z-**4a** and Z-**4c** geometrical isomers.

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