J. Am. Chem. Soc. **2000,** *122,* 2132−2133

An Unusual Planar Diacyl Ditelluride ($(2\text{-}MeOC_6H_4COTe)_2$): The Origin of Its Planarity

Osamu Niyomura, Shinzi Kato,* and Satoshi Inagaki

Department of Chemistry, Faculty of Engineering
Gifu University, Yanagido, Gifu 501-1193, Japan

Received August 30, 1999
Revised Manuscript Received January 5, 2000

Since the first synthesis of diorganyl peroxides in 1858 by Brodie, who isolated dibenzoyl peroxide by reacting benzoyl chloride with Na_2O_2,[1] diacyl peroxides have been extensively investigated and widely used in industry.[2] In contrast, little is known about the chalcogen isologues **I** (136 different groups) in which the carbonyl or peroxide oxygens are replaced by sulfur, selenium, or tellurium (Scheme 1). Among them, diacyl ditellurides were not isolated until our report in 1987 of bis(2-methoxybenzoyl) ditelluride due to their extreme instability.[3,4] In general, diorganyl peroxides and higher dichalcogenides R−E−E−R (E = O, S, Se or Te) have been shown to have dihedral angles of 80−110° around the E−E axis (skew conformation)[5,6] as a result of the electronic repulsion among the lone pair electrons of oxygen or higher chalcogen atoms.[7] No planar diacyl higher dichalcogenides have been reported, although several planar diorganyl peroxides are known.[5a] Recently, the importance of nonbonded intramolecular interactions has been recognized as a key factor that influences the structure, stability, and reactivity of organo main group element compounds.[8] We have tried to isolate other diacyl ditellurides, but failed. This prompted us to elucidate the nature of the stability of the isolable 2-methoxybenzene derivative. In this paper, we report the first crystallographic study of a diacyl ditelluride and the origin of its unusual planarity and stability.

To synthesize a diacyl ditelluride, a new method that involves alkali metal tellurocarboxylates and XeF_2 as an oxidizing agent was used.[5c,9] As expected, the oxidation of sodium 2-methoxybenzenecarbotelluroate with XeF_2 proceeded readily below −15 °C to give bis(2-methoxybenzoyl) ditelluride **1** in 76% yield as red crystals[10] (Scheme 2).

The structure of **1** determined by X-ray analysis is shown in Figure 1.[11] Surprisingly, the central part of the molecule is planar (dihedral angle C7−Te1−Te1′−C7′, 180.0°). Intramolecular nonbonded interactions were observed between the tellurium and the methoxy oxygen [Te1···O2, 2.765(9) Å] and between the tellurium and the opposite carbonyl oxygen [Te1···O1′, 3.11(1) Å], which are significantly shorter than the sum of the van der Waals radii of both atoms (3.58 Å).[12] Thus, the molecule is considered to be stabilized by both 1,5- and 1,4-type Te···O intramolecular interactions.[13] For comparison, we carried out an X-ray structural analysis of bis(2-methoxybenzoyl) disulfide **2** and diselenide **3**.[14] However, these molecules are not planar. They sustain dihedral angles C−E−E−C of 84.7(3)° for the disulfide **2** (E = S) and 79.5(2)° and 104.8(2)° for the diselenide **3** (E = Se).

To better understand this striking structural difference between ditelluride **1** and other dichalcogenides **2** and **3**, ab initio MO calculations were carried out. Geometry optimizations for the planar and skew conformers of bis(2-methoxybenzoyl) dichalcogenides (**1**, **2**, and **3**) were performed using the Gaussian 94 programs.[15] The calculations for the disulfide **2** and diselenide **3** indicated that the skew conformers are more stable than the planar conformers.[16] In sharp contrast, the ditelluride **1** adopts a planar conformation that is more stable than a skew conformation.[17] These results are consistent with the results obtained by X-ray structural analyses of **1**, **2**, and **3**, i.e., the disulfide **2** and diselenide **3** assume a skew conformation, whereas the ditelluride **1** exists as a planar conformer. To obtain further information regarding the electronic structures of **1**, **2**, and **3**, NBO (natural bond orbital) analyses[18] were carried out. The results of a deletion energy analysis[19] are shown in Table 1. For all conformers of the dichalcogenides **1**, **2**, and **3**, attractive interactions between the lone pair of the ortho methoxy oxygen and chalcogen atoms were observed. This is likely to contribute to the overall stability of

---

* To whom correspondence should be addressed. E-mail: shinzi@apchem.gifu-u.ac.jp.

(1) Brodie, B. C. *Ann.* **1858**, *108*, 79−83.

(2) *The Chemistry of Organic Peroxides*; Patai, S., Rappoport, Zvi., Eds.: John Wiley & Sons: New York, 1983, and references therein.

(3) (a) Kakigano, T.; Kanda, T.; Ishida, M.; Kato, S. *Chem. Lett.* **1987**, 475−478. (b) Suzuki, H.; Inamasu, T.; Ogawa, T.; Tani, H. *J. Chem. Res. (S)* **1990**, 56−57.

(4) $(Me_2NCOTe)_2$ having −COTeTeCO− moiety has been reported (C−Te−Te−C: 88.5°): Zingaro, R. A.; Herrera, C.; Meyers, E. A. *J. Organomet. Chem.* **1986**, *306*, C36−C40.

(5) The X-ray structures of $(RCOE)_2$ which adopt skew confomation have been reported. (a) For example $(PhCOO)_2$: Sax, M.; McMullan, R. K. *Acta Crystallogr.* **1967**, *22*, 281−288. McBride, J. M.; Vary, M. W. *Tetrahedron* **1982**, *38*, 765−775. There is an exceptional dihedral angle of 180.0° for $(Ph_3CCH_2COO)_2$: Walter, D. W.; McBride, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 7074−7084. (b) $(PhCOS)_2$: Rout, G. C.; Seshasayee, M.; Subrahamanyan, T.; Aravamudan, G. *Acta Crystallogr.* **1983**, *C39*, 1387−1389. (c) $(4\text{-}MeOC_6H_4COSe)_2$: Niyomura, O.; Tani, K.; Kato, S. *Heteroatom Chem.* **1999**, *10*, 373−379.

(6) A Cambridge Structural Database search for the molecules of nonplanar diorgano ditellurides containing C−Te−Te−C groups resulted in 22 hits with the C−Te−Te−C torsion angles in the range 72.4−145.0°.

(7) For example, the S−S bond: (a) Steudel, R. *Angew. Chem.* **1975**, *87*, 683−720. (b) The $n_S-\sigma^*_{SC}$ interaction: Chou, J.-H.; Rauchfuss, T. B.; Szczepura, L. F. *J. Am. Chem. Soc.* **1998**, *120*, 1805−1811 and references therein.

(8) For example, see: (a) Barton, D. H. R.; Hall, M. B.; Lin, Z.; Parekh, S. I.; Reibenspies, J. *J. Am. Chem. Soc.* **1993**, *115*, 5056−5059. (b) Minyeav, R. M.; Minkin, V. I. *Can. J. Chem.* **1998**, *76*, 776−788. Reviews concerning tellurium−oxygen (or nitrogen) interactions: (c) McWhinnie, W. R. *Phosphorus Sulfur and Silicon* **1992**, *67*, 107−123. (d) Sudha, N.; Singh, H. B. *Coord. Chem. Rev.* **1994**, *135/136*, 469−515. (e) McWhinnie, W. R.; Sadekov, I. D.; Minkin, V. I. *Sulfur Rep.* **1996**, *18*, 295−335.

(9) Niyomura, O.; Kitoh, Y.; Nagayama, K.; Kato, S. *Sulfur Lett.* **1999**, *22*, 195−207.

(10) The corresponding sulfur **2** and selenium isologues **3** show colorless and pale yellow, respectively. However, regular bathochromic shifts of their λ_{max} in dichloromethane are not observed (see the Supporting Information).

(11) Crystal data and packing diagrams for **1**, see the Supporting Information.

(12) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(13) No example of a 1,4-nonbonded C═O···Te(II) interaction has been reported, although several compounds having 1,5- and 1,6-type C═O···Te(II,IV)[8] and 1,4-C═O···Te(IV) interactions have been discussed in the literature: (a) Sato, S.; Kondo, N.; Horn, E.; Furukawa, N. *Organometallics* **1998**, *17*, 1897−1900. (b) Matano, Y.; Suzuki, H.; Azuma, N. *Organometallics* **1996**, *15*, 3760−3765. (c) Drake, J. E.; Khasrou, L. N.; Mislankar, A. G.; Ratnani, R. *Inorg. Chem.* **1994**, *33*, 6154−6162. (d) Drake, J. E.; Drake, R. J.; Khasrou, L. N.; Mislankar, A. G.; Ratnani, R.; Yang, J. *Can. J. Chem.* **1996**, *74*, 1968−1982.

(14) Crystal data for **2** and **3**: see the Supporting Information: As expected, intramolecular interactions are observed between the methoxy oxygen and the sulfur [S···OMe: 2.666(4) and 2.654(4) Å] or the selenium [Se···OMe: 2.686(3) and 2.670(3), 2.623(3) and 2.708(3) Å]. The distances between the carbonyl oxygen and the opposite S or Se atoms are 2.960(5) and 2.977(5) Å for disulfide and 3.161(3), 3.133(3), 3.143(3), and 3.108(3) Å for diselenide. Although these distances are fairly short, NBO analyses suggest there is no attractive interaction between these atoms (see Table 1).

(15) See the Supporting Information.

(16) The dihedral angles θ (C−E−E−C) of the optimized skew conformers of the disulfide and diselenide are 68.7 [70.7] and 69.6 [71.4]°, respectively, at the RHF/LANL2DZ [B3LYP/LANL2DZ] levels. The skew conformers are more stable than the planar conformers by 3.0 [1.1] kcal/mol for disulfide and 1.2 [0.092] kcal/mol for diselenide.

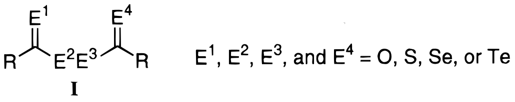
(17) The planar conformers of the ditelluride are more stable than the skew conformers (θ = 75.7 [84.5]°) by 2.4 [2.1] kcal/mol.

(18) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736−1740. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

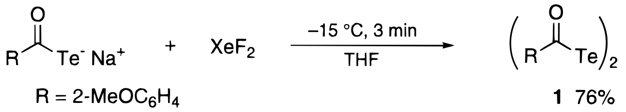
(19) (a) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1996**, *118*, 8077−8084. (b) Komatsu, H.; Iwaoka, M.; Tomoda, S. *J. Chem. Soc., Chem. Commun.* **1999**, 205−206.

10.1021/ja993120j CCC: $19.00

Scheme 1



Scheme 2



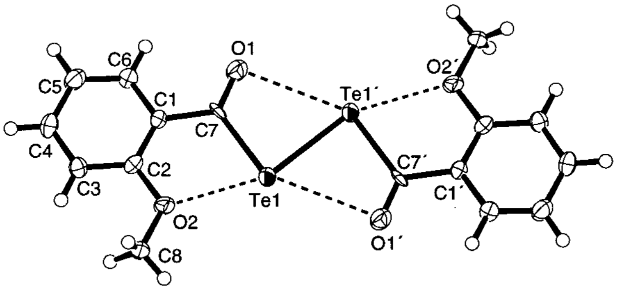


Figure 1. An ORTEP drawing of bis(2-methoxybenzoyl) ditelluride **1**. The atoms are drawn with 50% probability thermal ellipsoids. Selected bond distances (Å), angles (deg), and torsion angles (deg): Te1−Te1′ 2.739(2), Te1−C7 2.15(1), O1−C7 1.18(1), Te1···O2 2.765(9), Te1···O1′ 3.11(1), Te1′−Te1−C7 87.0(3), Te1−C7−O1 120.0(10), C2−O2−C8 119(1), Te1′−Te1···O2 158.0(2), C7−Te1−Te1′−C7′ 180.0, Te1−C7−C1−C2 8(1), Te1′−Te1−C7−O1 2(1).

Table 1. Results of NBO Analysis on Skew and Planar Conformer Dichalcogenides (Deletion Energy, *E* [kcal/mol]) at RHF/LANL2DZ [B3LYP/LANL2DZ] Levels

		E		
$(2\text{-MeOC}_6\text{H}_4\text{COE})_2$		S	Se	Te
n_O(methoxy) $\rightarrow \sigma^*_{E-E}$	skew	4.33 [6.24]	5.71 [7.84]	6.66 [9.01]
	planar	4.97 [7.22]	6.10 [8.61]	6.20 [8.75]
$n_E \rightarrow \sigma^*_{E-C}$	skew	3.40 [2.79]	3.49 [3.01]	3.49 [3.25]
	planar	−0.01 [0.03]	0.02 [0.03]	0.13 [0.16]
n_O(carbonyl) $\rightarrow \sigma^*_{E-C}$	skew	0.01 [0.00]	0.01 [−0.01]	0.04 [0.00]
	planar	1.51 [1.79]	1.89 [2.07]	2.77 [3.04]

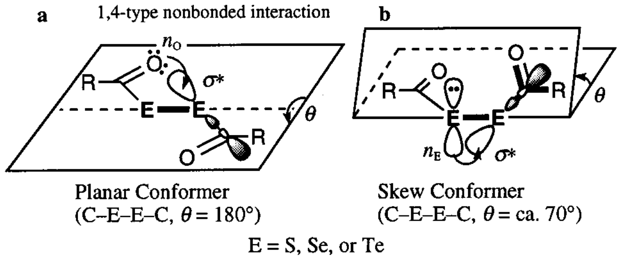


Figure 2. Possible explanation of the nonbonded interaction due to n_O−σ^* (planar conformer) and n_E−σ^* orbital overlap effect (skew conformer).

the molecules. Orbital interactions between the lone pair of the chalcogen atom (n_E) and the σ^*_{EC} orbital is present for skew conformations (Figure 2, **b**), but their values are close. On the other hand, orbital interactions between the lone pair of the carbonyl oxygen (n_O) and the σ^*_{EC} orbital (1,4-interaction[20]) are observed only for planar conformers (Figure 2, **a**). Notably, the deletion energy of ditelluride **1** corresponding to this interaction is the largest among these three dichalcogenides. This may substantially contribute to the stabilization of the planar conformer of **1**, and may also result in shortening of the distance between Te···O=C as has been observed by X-ray molecular structural analysis.

We compared orbital energies and the magnitude of the contributions of atomic orbitals to σ^*_{EC} for the dichalcogenides.[21] First, the orbital energies of the lone pair of the carbonyl oxygen in the dichalcogenides are nearly equal, whereas the energy of the σ^*_{TeC} orbital is the lowest among the three σ^*_{EC} (E = S, Se, or Te) orbitals. Thus, the energy gap between n_o (donor) and σ^*_{TeC} (acceptor) is the smallest among the three compounds, and the stabilization due to orbital interaction is the greatest. Second, the contribution of the tellurium atomic orbital to the σ^*_{TeC} orbital is the highest among the three compounds, i.e., the σ^*_{TeC} orbital extends to the lone pair of the carbonyl oxygen, resulting in stronger contact with the lone pair on the carbonyl oxygen. Accordingly, the orbital interaction between the lone pair of the carbonyl oxygen n_o and the σ^*_{TeC} orbital is maximized in these three dichalcogenides in terms of (i) orbital energy and (ii) orbital overlap. This effect may play an important role in the planar conformation of ditelluride **1** together with the interaction between the lone pair orbital of the methoxy oxygen and the Te−Te antibonding orbital. The significance of the n−σ^* interactions proposed here is substantiated by the observed planar geometry of bis(3-chloro-2-pyridyl) ditelluride.[22] The lone pairs of the nitrogen and chlorine atoms in place of the carbonyl and methoxy oxygens in **1** similarly delocalize to the Te−C and Te−Te bonds, respectively.

In summary, the first stacked planar diacyl dichalcogenide, $(2\text{-MeOC}_6\text{H}_4\text{CO})_2\text{Te}_2$, was synthesized and characterized. We found that intramolecular nonbonded interactions between the carbonyl oxygens and the tellurium atoms play a more important role in its planarity rather than those between the methoxy oxygens and the tellurium. These findings may not only contribute to the design of chalcogen containing planar molecules, especially new organo electronic materials requiring planarity, but also lead to the synthesis of many other unstable higher chalcogen isologues of diacyl peroxides.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 09239220) and by Grants-in-Aid for Scientific Research (No. 09355032) from the Ministry of Education, Science, Sports and Culture of Japan. We thank Prof. Takashi Kawamura and Associate Prof. Masahiro Ebihara of Gifu University for invaluable assistance with the X-ray crystallography.

Supporting Information Available: Experimental details for **1**, X-ray structural information for **1**−**3** including atomic coordinates and isotropic thermal parameters, and calculated coordinates for the planar and skew conformer of **1**−**3** (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JA993120J

---

[20] For $HX-CH_2-CHO$ (X = S, Se, Te), the lowest energy conformers have twist conformation with the absence of a 1,4-type X···O=C interaction: Markham, G. D.; Bock, C. L.; Trachtman, M.; Bock, C. W. *J. Mol. Struct. (THEOCHEM)* **1999**, *459*, 187−199.

[21] See the Supporting Information (Table S8).

[22] Junk, T.; Irgolic, K. J.; Meyers, E. A. *Acta Crystallogr.* **1993**, *C49*, 975−976.