Table 4. *Assigned chemical shifts for methylene protons in rings B, C and D of GF* (*on δ scale in* $CDCl_3$)

Proton	δ	Proton	δ
$H6_\alpha$	2·48	$H14_\alpha$	1·52
$H6_\beta$	1·84	$H14_\beta$	1·45
$H7_\alpha$	1·99	$H15_\alpha$	2·18
$H7_\beta$	1·45	$H15_\beta$	2·60
$H12_\alpha$	2·42	$H17_c$*	4·89
$H12_\beta$	1·98	$H17_t$†	4·78

* *cis* to C13.
† *trans* to C13.

the dramatic conformational differences between GF and KA. The adoption of the boat conformation by ring *B* of GF must change the rotation of the (−)-kaurene skeleton from negative to positive.

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Structure of Bis(*p*-methoxyphenyltelluro)ethyne

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Abstract. $C_{16}H_{14}O_2Te_2$, $M_r = 493{\cdot}3$, monoclinic, $P2_1/n$, $a = 7{\cdot}911\ (3)$, $b = 6{\cdot}671\ (6)$, $c = 15{\cdot}443\ (4)$ Å, $\beta = 95{\cdot}4\ (4)^\circ$, $V = 811{\cdot}1$ Å^3, $Z = 2$, $D_x = 2{\cdot}02$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}70926$ Å, $\mu = 36{\cdot}02$ cm^{-1}, $F(000) = 460$, room temperature, $R = 0{\cdot}051$, $wR = 0{\cdot}053$ for 1429 observed reflections [$I \geq 2{\cdot}5\sigma(I)$]. The structure is characterized by centrosymmetric binuclear molecules linked through the acetylenic moiety, with four atoms almost linear: Te(1)—C(1)—C(1*)—Te(1*).

Introduction. The use of organotellurium derivatives as reagents and intermediates in organic synthesis has been reviewed (Petragnani & Comasseto, 1986). We have been interested in the insertion reaction of reactive intermediates like carbenes and diacetylides in the Te—Te bond of diaryl ditellurides. In an attempt to understand their chemistry more fully and especially to use the new products in organic synthesis, we report here the synthesis of the title compound, prepared for the first time, by reaction of arenetellurenyl bromides, generated *in situ*, with di-Grignard reagents.

Procedures described in the literature were followed to synthesize all the reagents: bis(*p*-methoxyphenyl) ditelluride (Reichel & Kirschbaum, 1943), *p*-methoxyphenyltellurenyl bromide (Petragnani, Torres, Wynne & Maxwell, 1973;

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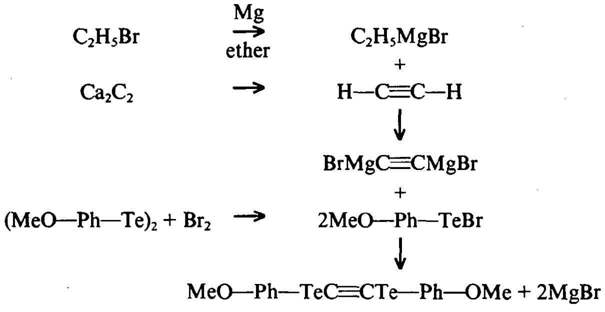
Petragnani, Torres, Wynne & Williams, 1974), acetylene (Addison, Hobdell & Pulham, 1971) and acetylenedimagnesium dibromide (Isler, Lindlar, Montavon, Rüegg & Zeller, 1956; Kranzfelder & Vogt, 1938).



Preliminary results about the Te—C(*sp*) bond cleavage in acetylenic tellurides using reducing agents have been reported (Dabdoub, Dabdoub, Comasseto & Petragnani, 1986) and, more recently, a study of the properties of the acetylenic tellurides as electrophilic or nucleophilic reagents was published (Dabdoub & Comasseto, 1988). A structural study of the title compound was undertaken in order to examine the bonding and molecular geometry in these types of intermediates.

Experimental. In a three-necked 100 ml flask fitted with a condenser, a nitrogen inlet, a liquid addition funnel and a magnetic stirrer, an ethereal solution of ethylmagnesium bromide was prepared as usual, from ethyl bromide (0·05 mol), magnesium (0·048 mol) and freshly distilled THF (50 ml). When all the magnesium was dissolved the funnel was replaced by a gas inlet dipping into the solution, and acetylene was bubbled through it for 12 h with constant stirring. This solution, after titrating with HCl, was added with a syringe through a septum to a three-necked flask containing 0·015 ml of a brown–red solution of *p*-methoxyphenyltellurenyl bromide [prepared from bis(*p*-methoxyphenyl) ditelluride and bromine in benzene] maintained in an ice–water bath. The solution was stirred magnetically under a nitrogen atmosphere, until it was completely colorless. After stirring for a further hour at 288 K, the solution was diluted with petroleum ether and treated with aqueous ammonium chloride and saturated aqueous sodium chloride. The organic layer was separated and dried with anhydrous calcium sulfate, and the solvent evaporated; 3·38 g of a red semi-solid material was obtained. TLC gave four spots. The product was chromatographed through a column with silca gel G as adsorbent and petroleum ether mixtures of petroleum ether–methylene chloride as eluents (35% yield). Analysis: calc. for $C_{16}H_{14}O_2Te_2$: C, 38·95; H, 2·86; Te, 51·73%. Found: C, 38·70; H, 2·77; Te, 51·73%.

The yellow–green crystals of the product were recrystallized from methylene chloride/petroleum ether (40–60), m.p. 386–387 K. A crystal suitable for X-ray studies with dimensions 0·15 × 0·15 × 0·20 mm was selected. Enraf–Nonius CAD-4 diffractometer. Unit-cell parameters by least squares from 25 reflections with θ between 6 and 13°; 2850 reflections collected, 1429 unique, 1201 considered observed with $I \geq 2{\cdot}5\sigma(I)$; ω–2θ scan mode, *hkl* range: $-7 \leq h \leq 7$, $-9 \leq k \leq 9$, $0 \leq l \leq 19$, θ limit 25°; one standard measured every three reflections, ± 2·00% variation; scan range $\Delta\theta = (0{\cdot}80 + 0{\cdot}34\tan\theta)°$; standard reflection 213 showed no significant decay of intensity. Lorentz–polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN*11/84; Main, Germain & Woolfson, 1984). Heavy atoms and eight non-H atoms located in best *E* map, remaining non-H and H atoms by subsequent Fourier maps. Anisotropic full-matrix least-squares refinement of non-H atoms (*SHELX*76; Sheldrick, 1976), isotropic free-variable temperature-factor refinement for H atoms ($U = 0{\cdot}0508$ Å^2). 1492 reflections included in final refinement cycle, 113 parameters refined; $R = 0{\cdot}0507$, $wR = 0{\cdot}0527$, $w = 1{\cdot}000/[\sigma^2(F) + 0{\cdot}00752F^2]$; max. $(\Delta/\sigma) = 0{\cdot}66$ for a methyl H atom. Atomic scattering factors (except tellurium) from *International Tables for X-ray Crystallography* (1974, Vol. IV); scattering factors for tellurium from Forsyth & Wells (1959). Residual electron density within $\pm 1{\cdot}9$ e Å^{-3} near the Te atom. Drawing by *PLUTO* (Motherwell & Clegg, 1978). All calculations were performed on a Digital MicroVAXII.

Discussion. The atomic parameters are given in Table 1.† A view of the molecule with the atomic numbering scheme is shown in Fig. 1. Table 2 gives bond distances and angles. The molecular packing in the crystal is illustrated in Fig. 2.

In the centrosymmetric binuclear molecule of the title compound, the acetylenic moiety and the two Te atoms bonded to it form an almost linear sequence, Te—C(1)—C(1*) = 178·1°. The acetylenic C(1)—C(1*) bond length, 1·210 (11) Å, is very close to the value of 1·2033 (2) Å found for C≡C in acetylene (Fast & Welsh, 1972; van Nes & van Bolhius, 1979) and may be compared with 1·174 (10) Å found in *p*-chlorophenyl(phenylseleno)acetylene (Husebye,

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† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53348 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$, $\times 10^5$ *for* Te) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

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

	x	y	z	B_{eq}
Te(1)	78473 (5)	21714 (8)	8133 (3)	4·04
C(1)	9493 (7)	485 (8)	182 (4)	3·99
C(11)	6774 (7)	3540 (9)	− 341 (4)	3·76
C(12)	7289 (7)	5404 (9)	− 578 (4)	4·12
C(13)	6551 (8)	6320 (9)	− 1346 (5)	4·59
C(14)	5334 (7)	5361 (9)	− 1868 (5)	4·30
C(15)	4831 (9)	3396 (10)	− 1619 (5)	4·68
C(16)	5514 (8)	2551 (9)	− 855 (5)	4·19
O(1)	4591 (6)	6039 (8)	− 2629 (3)	5·10
C(17)	5173 (11)	7910 (10)	− 2946 (6)	6·73

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—Te(1)	2·037 (5)	C(14)—C(15)	1·432 (8)
C(11)—Te(1)	2·109 (6)	C(15)—C(16)	1·372 (10)
C(1)—C(1*)	1·210 (11)	C(16)—C(11)	1·382 (9)
C(12)—C(11)	1·369 (8)	C(14)—O(1)	1·343 (9)
C(12)—C(13)	1·412 (10)	C(17)—O(1)	1·433 (8)
C(13)—C(14)	1·355 (9)	Te(1)···O(1^i)	3·41 (4)

C(11)—Te(1)—C(1)	93·4 (2)	C(13)—C(14)—C(15)	118·2 (6)
C(12)—C(11)—Te(1)	120·8 (5)	C(13)—C(14)—O(1)	126·1 (6)
C(16)—C(11)—Te(1)	119·3 (5)	C(16)—C(15)—C(14)	120·6 (6)
C(13)—C(12)—C(11)	120·5 (6)	C(15)—C(16)—C(11)	120·1 (6)
C(16)—C(11)—C(12)	119·8 (6)	C(17)—O(1)—C(14)	117·7 (6)
C(12)—C(13)—C(14)	120·6 (6)	C(11)—Te(1)···O(1^i)	166·2 (2)

Symmetry code: (i) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$.

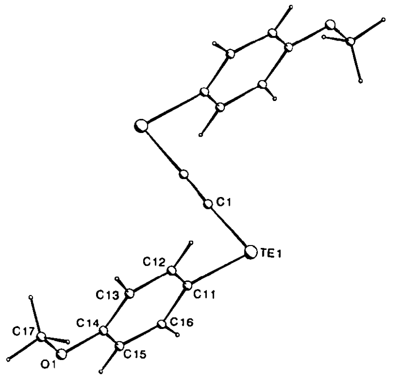

Fig. 1. A view of the molecule showing the atomic numbering.

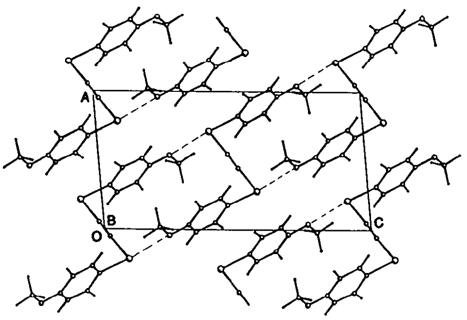

Fig. 2. Projection of the structure along the *b* axis showing intermolecular contacts (broken).

Meyer, Zingaro, Braga, Comasseto & Petragnani, 1986). The Te—C(1) distance, 2·037 (5) Å, similar to that observed for 4-nitrobenzyltellurocyanate, 2·060 Å, (Maartmann-Moe, Sanderud & Songstand, 1984), is shorter than that predicted from the sum of single covalent radii for Te—C(*sp*) 2·057 Å (Foss, 1962; Bastiansen & Traetteberg, 1962), being indicative of the presence of some double-bond character. The Te—C(11) bond length is comparable to that found for diphenyl ditelluride, 2·081 (18) Å (Llabres, Dideberg & Dupont, 1972), and agrees with the average Te—C single bond in Ph_2TeX_2 (Alcock & Harrison, 1982). The C(1)—Te—C(11) angle, 93·4 (2)°, is within the range found in other divalent compounds: 94 (1)° in *p*-dichlorodiphenyl ditelluride (Kruse, Marsh & McCullough, 1957), 90·6 (1)° in 4-nitrobenzyltellurocyanate (Maartmann-Moe *et al.*, 1984) and 94 (2)° for dimethyltellurium (Blom, Haaland & Seip, 1983). An intermolecular contact, Te···O(1^i), approximately *trans* to the Te—C(11) bond, at a distance of 3·41 (4) Å [shorter than the sum of the van der Waals radii, 3·58 Å (Bondi, 1964)], is present in the crystal structure. If this interaction is included, the configuration around the tellurium atom may be regarded as pseudo-square planar, with the fourth position vacant.

In terms of three-center two-electron bonds (Foss, 1970), the reactivity of the title compound should be related to the ability of the reagent to engage the 5*p* orbital of the tellurium atom at the expense of the Te—C(*sp*) bond (at 180° to the incoming group).

The phenyl ring is planar within experimental accuracy [r.m.s. deviation = 0·011 Å; δ_{max} = 0·018 Å for C(15) and C(16)]. The bond lengths and angles in the phenyl ring are within the expected range of values.

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Azoles. 30.* Structure of the Molecular Complex of 3,5-Dinitroindazole with Thiomorpholine (1/1)

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Abstract. $(C_7H_4N_4O_4.C_4H_9NS)_2$, $M_r = 622\cdot63$, monoclinic, $C2/c$, $a = 20\cdot751\,(3)$, $b = 6\cdot782\,(1)$, $c = 20\cdot339\,(3)$ Å, $\beta = 102\cdot99\,(1)°$, $V = 2789\cdot3\,(7)$ Å^3, $Z = 4$, $D_m = 1\cdot48\,(1)$, $D_x = 1\cdot48$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot54178$ Å, $\mu = 2\cdot175$ mm^{-1}, $F(000) = 1296$, room temperature, final $R = 0\cdot040$ for 1417 reflections. The molecular complex of 3,5-dinitroindazole and thiomorpholine lies on the 2 axis. The thiomorpholine molecule forms an $H_2N^+\!<$ ammonium cation as a result of the incorporation of a proton from the pyrrole N atom of the indazole moiety. The indazole system is approximately planar. The thiomorpholinium cation has a chair conformation; its least-squares plane makes a dihedral angle of 91·3 (1)° with the plane of the indazole system. Molecules in the complex are hydrogen bonded.

Introduction. In our preceding papers we described the X-ray structures of the molecular complexes of 3,5-dinitroindazole with morpholine [(I), Gzella, Wrzeciono & Borowiak, 1989], pyrrolidine [(II), Gzella & Wrzeciono, 1990] and piperazine [(III), Gzella & Wrzeciono, 1991]. This paper deals with the structure of the molecular complex of the same indazole derivative with thiomorpholine.

Experimental. The title compound, m.p. 475–476 K, was prepared by treating 3,5-dinitroindazole with thiomorpholine according to the method described by Wrzeciono & Linkowska (1980), yellow needle crystals recrystallized from propanol/water solution, D_m by flotation, crystal dimensions 0·4 × 0·3 × 0·2 mm, Syntex $P2_1$ diffractometer, graphite-monochromated Cu $K\alpha$ radiation, accurate lattice parameters from setting angles of 15 reflections with $11° \leq 2\theta \leq 33°$, θ–2θ scan technique, two standard reflections monitored every 100 reflections, no significant intensity variation, 1819 unique reflections, $R_{\mathrm{int}} = 0\cdot022$, range of hkl: h −21 to 21, k 0 to 8, l 0 to 21, profile analysis according to Lehmann & Larsen (1974), 1417 reflections with $I \geq 1\cdot96\sigma(I)$ considered observed and used in the refinement, structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refinement on F by full-matrix least-squares method, semi-empirical absorption corrections using *DIFABS* (Walker & Stuart, 1983),

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* Part 29: Gzella & Wrzeciono (1991).

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