(*E*)/(*Z*) Equilibria, 13[1]

Molecular Structures of a Lithiated Schiff Base and a Related Dialkyl Ketone Imine

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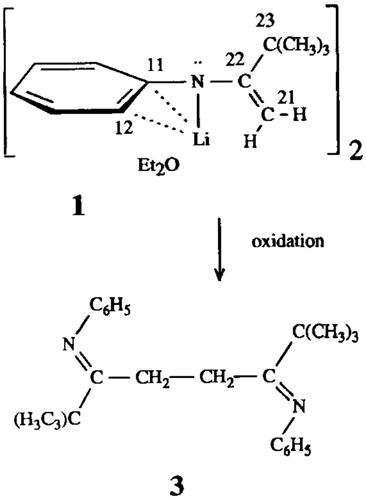
The ether-solvated lithium derivative of pinacolone anil (**2a**) is shown to be a centrosymmetric dimer (**1**) by X-ray diffraction analysis. Each lithium atom is bound to two nitrogen atoms, to the oxygen atom of diethyl ether, and weakly to two carbon atoms of a phenyl ring, but not to the vinyl moiety of the enamide anion. Despite conformational deconjugation, **1** is methylated at the carbon atom by methyl iodide. ^{1}H-NMR shifts of **1** in solution are solvent-dependent. The results are discussed with respect to the "*syn* effect" in 1-azaallyl anions. The molecular structure of the dianil **3** of 2,2,7,7-tetramethyl-3,6-octanedione shows that a CH proton may approach the π face of an aromatic carbon atom down to a nonbonding distance of 2.74 Å without causing much strain.

1-Azaallyllithium compounds are important enolate equivalents and have frequently been studied[3]. Consideration of their molecular topology and conformation could provide a basis for the rationalization of stereoselective reactions, especially chiral induction[4–6], but had to be based on indirect evidence obtained from chemical, computational and spectroscopic results[7,8] in solution, until the first single-crystal analyses[9–11] became available. During experimentation[12,13] with metalated Schiff bases by low-temperature ^{1}H-NMR spectroscopy[13], a member (**1**) of this series was found suitable for X-ray diffraction analysis; in this paper its surprising structure[9] will now be presented in detail.

The structures of several related lithium derivatives[14] have been excluded from our consideration, because they were thought not to bear sufficiently on the conformational problem addressed in this work. The majority of these concern lithium enamides with restricted conformational choices due to their incorporation into aromatic rings. On the other hand, the structurally known lithiated hydrazones appear to be conformationally biased by intramolecular coordination to additional donor atoms.



1

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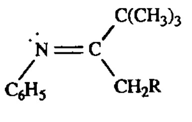

2a: R = H
b: R = CH$_3$

A deteriorated sample of **1** furnished the 1,4-dianil **3** which was also analyzed by X-ray diffraction and turned out to be a structural prototype for an anil of a saturated dialkyl ketone.

A. *N*-(2,2-Dimethyl-1-methylenepropyl)-*N*-lithiobenzenamine (1), a Dimeric Lithiated Schiff Base

The title compound **1** was prepared as before[13] from pinacolone anil (**2a**) with slight modifications. The atomic parameters are given in Table 5, the distances and angles in Table 1.

Figure 1 displays a stereoscopic view of the complex molecule **1** which possesses a crystallographic inversion centre. Therefore, the central N–Li–N′–Li′ quadrangle is planar and carries all its chemically equivalent ligand pairs in *trans* positions. Each lithium atom is bound to one oxygen atom of diethyl ether at a distance which is comparable to that in **5**[11] (Section B) and intermediate between those of the addition compounds of ether with lithium dibenzylamide[15] and lithium 2,4,6-tri-*tert*-butylanilide[16]. The O–Li bond forms an angle of 19.2° with the C(1)–O–C(3) plane, showing that the oxygen atoms are pyramidal. Both oxygen atoms are 0.221 Å off the N–Li–N′–Li′ plane; Li is thus only 0.088 Å above the triangle O–N–N′, and this elevation indicates an attraction of Li towards C(11) and C(12) which are 1.221 and 2.328 Å above that triangle. The coordinated ether is similar to the triethyloxonium ion[17] in its

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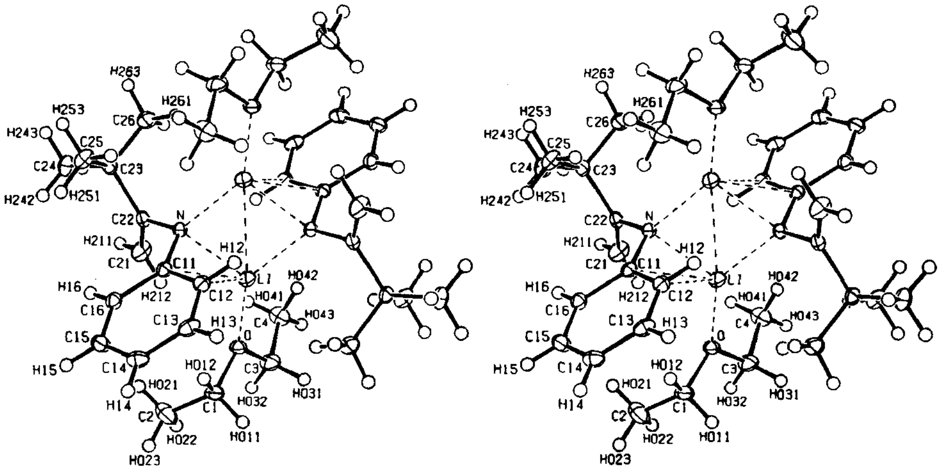


Figure 1. Stereoscopic view of the complex dimer of *N*-(2,2-dimethyl-1-methylenepropyl)-*N*-lithiobenzenamine (**1**) at 117 K with 50% probability ellipsoids except for hydrogen atoms which are represented by spheres of radius 0.1 Å

Table 1. Bond lengths [Å] and angles [°] of **1**, with standard deviations in units of the last significant figure in parentheses

Li-Li′	2.544(2)	C(1)-C(2)	1.503(2)	C(14)-C(15)	1.396(2)
O-Li	1.937(2)	C(3)-C(4)	1.490(2)	C(15)-C(16)	1.376(1)
O-C(1)	1.446(1)	C(11)-Li	2.437(2)	C(21)-C(22)	1.326(1)
O-C(3)	1.440(1)	C(11)-C(12)	1.422(2)	C(22)-C(23)	1.531(1)
N-Li	2.076(2)	C(11)-C(16)	1.417(1)	C(23)-C(24)	1.539(2)
N-Li′	2.000(2)	C(12)-Li	2.662(2)	C(23)-C(25)	1.526(1)
N-C(11)	1.380(1)	C(12)-C(13)	1.381(1)	C(23)-C(26)	1.529(1)
N-C(22)	1.436(1)	C(13)-C(14)	1.386(2)		

O-Li-N	121.93(9)	C(11)-C(12)-C(13)	121.94(9)
O-Li-N′	134.7(1)	C(12)-C(13)-C(14)	121.4(1)
O-Li-Li′	169.8(1)	C(13)-C(14)-C(15)	117.80(8)
N-Li-N′	102.78(7)	C(14)-C(15)-C(16)	121.4(1)
Li-N-Li′	77.22(7)	C(11)-C(16)-C(15)	122.07(9)
C(11)-N-Li	87.28(7)	C(22)-C(21)-H(211)	123.7(5)
C(11)-N-Li′	119.36(7)	C(22)-C(21)-H(212)	123.6(5)
C(22)-N-Li	117.87(6)	H(211)-C(21)-H(212)	112.7(7)
C(22)-N-Li′	122.53(7)	N-C(22)-C(21)	120.98(9)
C(11)-N-C(22)	116.61(7)	N-C(22)-C(23)	115.94(6)
C(1)-O-Li	119.66(7)	C(21)-C(22)-C(23)	122.95(9)
C(3)-O-Li	122.97(7)	C(22)-C(23)-C(24)	111.74(7)
C(1)-O-C(3)	113.22(7)	C(22)-C(23)-C(25)	110.49(7)
O-C(1)-C(2)	112.04(8)	C(22)-C(23)-C(26)	109.17(8)
O-C(3)-C(4)	108.85(8)	C(24)-C(23)-C(25)	108.60(8)
N-C(11)-C(12)	118.91(8)	C(24)-C(23)-C(26)	107.79(7)
N-C(11)-C(16)	125.74(8)	C(25)-C(23)-C(26)	108.99(7)
C(12)-C(11)-C(16)	115.30(8)	C(21)-C(22)-N-Li	20.9(1)
C(21)-C(22)-C(23)-C(24)	16.2(1)	C(21)-C(22)-N-C(11)	-80.9(1)

C(1)–O–C(3) bond angle (113°) but closer to the free diethyl ether molecule[18] in its C–O bond lengths.

The phenyl ring is perfectly planar as shown by the small mean square root deviation (0.0016 Å) of its carbon atoms from their common plane. Since also N and C(22) deviate only slightly from that plane, this whole atomic array meets the topological conditions for a charge-delocalized lithium anilide, even at the expense of forcing C(22) into the ring plane with the short distance of 2.854(1) Å from C(16). The resulting partial double-bond character of the N–C(11) bond is reflected by its length 1.380(1) Å. It causes an increased weight of the *p*-quinonoid resonance structure of the phenyl ring, as suggested by the reduced intraannular angles (Table 1) at C(11) and C(14) and the widened angles at C(12), C(16), C(13), and C(15).

Figure 2 shows the dimer **1** in a view parallel to the planes of the anilide anions, which clarifies their relation to the lithium cations. The metalated equatorial sp^2 nitrogen lone pair, on which the negative charge should be concentrated, forms a short bond to the equatorial Li′, which is almost coplanar (−0.353 Å) with the anilide plane, showing dihedral angles C(22)–N–C(11)–C(16) = 2.0(1)° and C(22)–N–C(11)–C(12) = 179.22(7)°. The axial Li is bound to the delocalized π surface below the triangle N–C(11)–C(12). This latter bond type is also observed in benzyllithium[19] (Li–C 2.21, Li–C_{ipso} 2.39, Li–C_{ortho} 2.59 Å) and many related structures. There is no coordination to the C(21)–C(22) double bond (see Section B).

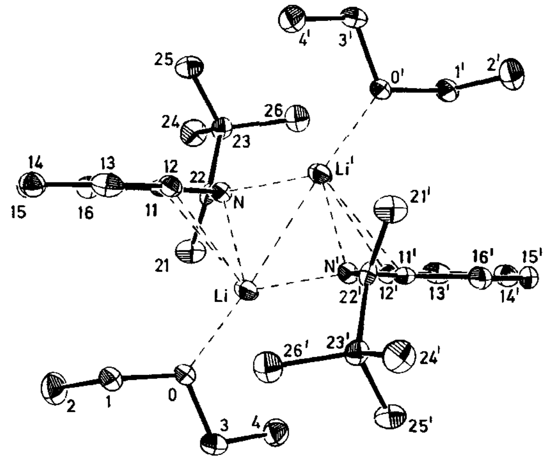


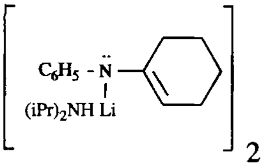
Figure 2. Heavy-atom skeleton of the dimeric lithio-enamide (addition compound with diethyl ether) **1**; the lateral view on the phenyl groups (atoms 11–16) illustrates the conformational π decoupling of the double bond C(21)–C(22) from the planar anilide fragment C(22)–N–C(11–16)

The methylene hydrogen atom H(211) in Figure 1 has a rather short distance from H(241) in the background of the *tert*-butyl group, whereas all intermolecular H···H distances are larger than 2.39 Å. An analysis of the methyl hydrogen positions reveals that this causes a 2.5° methyl rotation around the C(24)–C(23) bond. The methyl groups C(25) and C(26) have their sterically most favourable conformation, although there is a close contact [2.500(9) Å] of H(261) to Li′, which can also be recognized from Figure 1.

A comparison of **1** with the related structure of the addition compound of ether with lithium 2,4,6-tri-*tert*-butylanilide[16] is quite revealing. This, too, is a dimer with a crystallographic inversion centre and with an almost identical complex core $N_2Li_2O_2$. The *tert*-butylvinyl group in **1**, which is not engaged in the complex bonding, is replaced by a hydrogen atom, but strong sterical hindrance is introduced instead by *tert*-butyl groups in the two *ortho* positions of the ring. This is of course prohibitive for bonds from Li to C(11) and C(12). The resulting structural change can easily be understood with reference to Figure 2. Since the $N_2Li_2O_2$ core remains the same, the required large increase of the C(12)−Li distance is reached by a 20° rotation of the ring about its long N−C(14) axis and a widening of the C(11)−N−Li angle by 30°. The likewise necessary increase of the C(12)−Li′ distance is effected by a 30° rotation of the ring about the axial N−Li bond, expanding the C(11)−N−Li′ angle from its ideal value in **1** to 150.0(2)°. This exclusion of the ring from bonding to the axial lithium cation makes it plausible why the C(11)−N bond becomes slightly elongated to 1.394 Å in that structure[16] (decreasing interaction phenyl/N) and why both Li−N and Li−N′ bonds are slightly shortened instead.

B. The 1-Azaallyl Conformation in 1

The stereochemical situation in 1-azaallyl derivatives is a basic problem in the planning of stereoselective reactions[4−6,9] for the following reasons. Deprotonation of a Schiff base (**2a** in our case) requires that the developing 1-azaallyl anion should at least approximately conserve the coplanar arrangement about the former C−N double bond. This topology would be stabilized by the naively expected π interaction of the vinyl group with N (azaallyl resonance) and by simultaneous π coordination of lithium to the N−C−C fragment. However, Li will be most strongly bound to the more negative nitrogen atom in the fully formed azaallyllithium molecule, with the consequences of enhanced single-bond character and greater conformational freedom of the former C−N double bond. Therefore, subsidiary π coordination of the lithium cation may either be totally lost or be taken up with an *N*-aryl group. The latter two possibilities are realized in the deprotonated cyclohexanone anil **4**[10] and in **1**, respectively, while the 1-azaallyl structure has been only recently found in the conformationally fixed lithiated anil **5**[11] (which would result by tying the phenyl group of **1** to the *tert*-butyl carbon atom).



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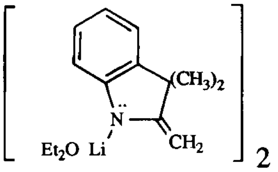

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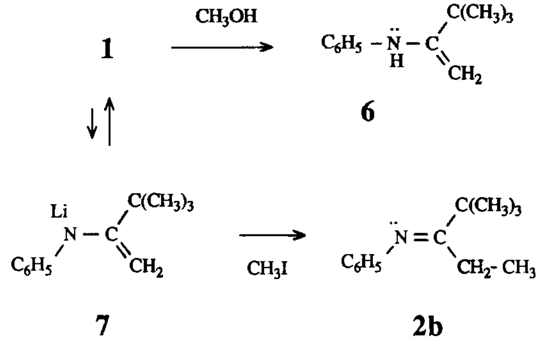
Figures 1 and 2 show that the bulky *tert*-butyl group in **1** precludes a coplanar conformation of the vinyl group with the N−phenyl bond; the dihedral angle C(11)−N−C(22)−C(21) is −80.9(1)° (Table 1), thus rendering the azaallyl resonance unimportant. Accordingly, the N−C(22) bond is longer and the C(21)−C(22) double bond shorter than in enamines with averaged distances[20] of 1.400(23) Å and 1.345(15) Å, respectively. A comparison of bond lengths and angles reveals that **5**[11] has the geometry of an enamine, contrasting with a recently analyzed monomeric lithium enhydrazide[14] despite strong charge delocalization in both of these compounds.

Due to the deconjugated character of the vinyl group, its β-carbon atom C(21) is not activated for electrophilic attack in the usual manner of enamines and enolates. This may be one of the reasons why methanolysis occurs only at the nitrogen atom of **1** to give the metastable *sec*-enamine **6**. Such *N* protonation appears to be possible with almost all types of lithiated imines[4,12,13] and has diagnostic value[4].



The N−C(22) bond has to rotate by about 90° to give a more or less planar 1-azaallyl conformation **7** prior to electrophilic attack. We had no difficulty to trap **7** in diethyl ether with methyl iodide: Only the anil **2b**, but no *N*-methylated products could be detected. This is in line with results[11] on the bona fide 1-azaallyl compound **5** as well as with the usual *syn* alkylation observed even with configurationally labile *N*-aryl imines[21] other than **2a**. Some synthetic implications of the dimeric structure have been discussed[9], but since the required planarization appears difficult to achieve within the dimer **1**, it could be suspected[10] that the "*syn* effect"[22] might operate in an intermediate (like a monomeric **7**) rather than in ground states like **1** or **4** (if retained in solution).

The published behaviour of **4**[8,10] and **5**[11] in solution suggests that dissolved **1** should likewise remain dimeric in diethyl ether but tend to deaggregate in THF. Since we have not applied similarly thorough[8,10] and sophisticated[11] methods of investigation to **1**, we have listed the relatively strong solvent dependencies of some of its ^{1}H-NMR chemical shifts in Table 2, which supplements our earlier[13] report. The insufficiently stable enamine **6** cannot be used as a reference due to uncertainties in its ^{1}H-NMR assignments. Taking the shifts of **1** in hexane solution for reference instead, the *p*-hydrogen signal moves upfield (by up to −0.84 ppm) much faster than the *o* and *m* signals in solvents of increasing ability for deaggregation and charge separation. This indicates rising π-charge densities in the phenyl ring and is expected. However, the shift increments for the olefinic β protons are seen to go through a positive maximum (downfield) in ether solution. We cannot offer an unequivocal explanation at this time but should like to note that the data presumably describe properties which are averaged over more than one molecular species. ^{13}C-NMR chemical shifts for **4**[8] and **5**[11] show a completely different and partially opposite behaviour.

Table 2. ^{1}H-NMR chemical-shift increments $\Delta\delta$ and olefinic geminal coupling constants $^2J_{HH}$ [Hz] of **1** in different solvents, referred to hexane solution

Solvent	*m*-H	*o*-H	*p*-H	β-H	β-H	$^2J_{HH}$
Hexane[a]	(6.97)	(6.67)	(6.47)	(4.12)	(4.05)	
Hexane	0	0	0	0	0	ca. 0
Diethyl ether	−0.12	−0.12	−0.35	+0.65	+0.28	1.0
Hexane/THF (4:1)	−0.32	−0.27	−0.67	+0.23	+0.03	1.1
THF	−0.44	−0.45	−0.84	+0.21	−0.03	2.3

[a] δ values.

Two final remarks may serve to compare **1** with other members of its class. The geminal olefinic ^{1}H-NMR coupling constants ^2J are similar for **1** and *N*-ethenyl-*N*-lithiocyclohexanamine (and solvent-dependent[13]), suggesting a similar σ-inductive effect[23] of the various N(Li)R substituents. On the other hand, the basicity of **1** roughly equals[13] that of LDA; therefore, **1** appears to be a stronger base than other 1-azaallyllithium derivatives[24].

C. The Dehydro Dimer (3) of Pinacolone Anil

The self-coupling product **3** was isolated from samples of **1** which had unintentionally been exposed to traces of dry air. Such oxidative dimerization may be related to the formation of 1,4-diketones from other lithiated imines with iodine[25]; however, oxygenation had previously been reported[26] to yield α-ketols. The well-crystallizing 1,4-dianil **3** offered a fortunate chance for X-ray diffraction analysis and a topological comparison of **1** and **3**.

Table 6 gives the atomic parameters and Figure 3 the stereo picture. The two halves of the molecule are related to each other by a crystallographic inversion centre on the newly formed CH_2-CH_2 bond which is, therefore, in the optimally staggered CC conformation. The C(2)−N double bond exhibits the (*E*) conformation, in accord with empirical substituent parameters[27] λ^d, and has dihedral twist angles C(1)−C(2)−N−C(11) = 4.48(5)° and C(3)−C(2)−N−C(11) = −179.94(3)°, corresponding to a smaller twist than in benzophenone *N*-acetylimine (7°)[28]. Its bond length and all of its bond angles, shown in Table 3, are very close to those of benzophenone *N*-(2,4,6-trimethylphenyl)imine[29] and of benzophenone anil[30]. Even the global topology of one half molecule of **3** resembles the topologies of the latter two compounds, probably because these have one copolanar and one nearly perpendicular C_6H_5 group corresponding in "size"[27] to the *tert*-butyl and CH_2-CH_2 substituents of **3**, respectively.

Table 3. **Bond lengths [Å] and bond angles [°] of 3**, with standard deviations in units of the last significant figure in parentheses

N-C(2)	1.2744(4)	C(3)-C(4)	1.5299(6)	C(12)-C(13)	1.3876(5)
N-C(11)	1.4257(5)	C(3)-C(5)	1.5349(5)	C(13)-C(14)	1.3848(5)
C(1)-C(1')	1.5445(5)	C(3)-C(6)	1.5417(6)	C(14)-C(15)	1.3915(7)
C(1)-C(2)	1.5261(6)	C(11)-C(12)	1.3992(6)	C(15)-C(16)	1.3914(5)
C(2)-C(3)	1.5279(5)	C(11)-C(16)	1.3917(5)		

C(2)-N-C(11)	120.53(3)	C(4)-C(3)-C(6)	108.92(3)
C(1')-C(1)-C(2)	111.38(3)	N-C(11)-C(12)	119.41(3)
N-C(2)-C(1)	123.96(3)	N-C(11)-C(16)	121.12(3)
N-C(2)-C(3)	118.76(3)	C(12)-C(11)-C(16)	119.35(3)
C(1)-C(2)-C(3)	117.27(3)	C(11)-C(12)-C(13)	120.32(3)
C(2)-C(3)-C(4)	111.40(3)	C(12)-C(13)-C(14)	120.33(3)
C(2)-C(3)-C(5)	110.94(3)	C(13)-C(14)-C(15)	119.46(3)
C(2)-C(3)-C(6)	107.35(3)	C(14)-C(15)-C(16)	120.67(3)
C(4)-C(3)-C(5)	108.45(3)	C(15)-C(16)-C(11)	119.83(3)

The conformation of **3** is completely governed by intramolecular sterical hindrance. Atom C(2) is perfectly planar (r.m.s.d. 0.006 Å) and the C(1)−C(1′) bond approximately perpendicular (ca. 81°) to this plane. The methylene group C(1) must obviously be in a *trans* relation [173.21(3)°] to one of the methyl groups [C(4)] of the *tert*-butyl moiety since otherwise there would be no space for H(1). The latter atom touches H(51) and H(61) at distances of 2.340(5) and

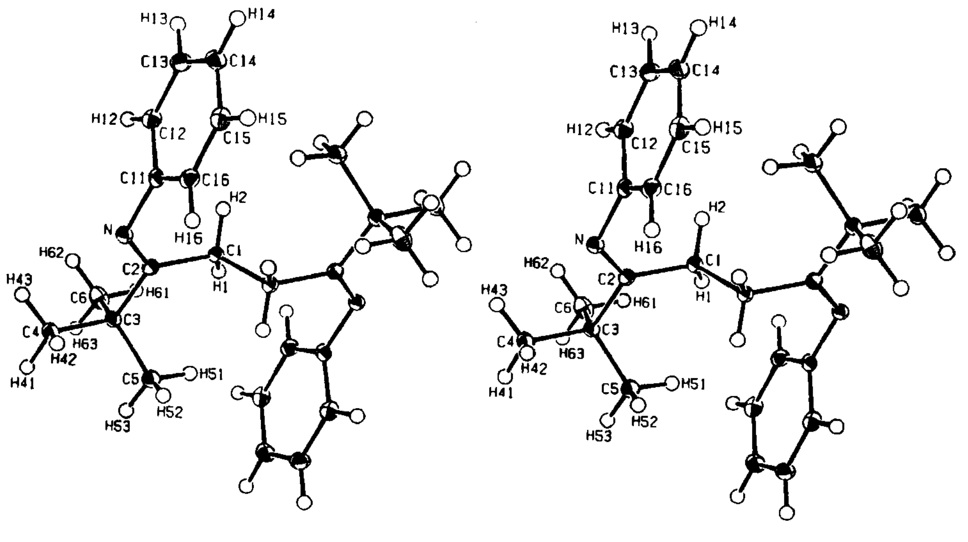


Figure 3. Stereoscopic view of the molecule *N*,*N*′-[1,4-bis(1,1-dimethylethyl)butane-1,4-diylidene]bis(benzenamine) (**3**) at 117 K with 50% probability ellipsoids except for hydrogen atoms which are represented by spheres of radius 0.1 Å

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2.196(4) Å, respectively. On the opposite side, the nitrogen atom is embedded with its lone pair above H(42) and H(43), the N···H distances being 2.666(3) and 2.636(3) Å, respectively.

The phenyl ring carbon atoms deviate by only 0.009 Å (r.m.s.d.) from their corresponding least-squares plane which forms an angle of 81.6° with the plane spanned about C(2). Judging from the dihedral angles C(2)−N−C(11)−C(12) = 81.07(4)° and C(2)−N−C(11)−C(16) = −103.07(4)°, the phenyl ring is not conjugated with the C(2)−N π system; its intraring bond angles show a very small spread (Table 3). The sense of twisting is away from C(1′), and a search for short nonbonded distances from C(11−16) in Table 4 shows that the phenyl ring has intramolecular contacts with both CH_2 groups and with H(51′) of the opposing *tert*-butyl group. This molecular conformation is certainly retained in solution, because the ^{1}H-NMR signal for *tert*-butyl is shifted upfield. There are also three intermolecular contacts to atoms H(53″), H(63″) and H(43‴) of neighbouring molecules, but these certainly cannot determine the phenyl conformation since they are outweighed by so many and shorter intramolecular ones.

Table 4. Nonbonded distances [Å] of the phenyl group in **3**

Phenyl	Contact	Distance	Phenyl	Contact	Distance
C(11)	C(1)	2.8530(7)	C(14)	H(51′)	2.951(3)
C(11)	C(1′)	3.4081(7)	C(15)	H(51′)	2.832(3)
C(11)	H(1′)	2.926(3)	C(15)	H(63″)	2.885(3)
C(12)	C(1)	3.3689(7)	C(15)	H(43‴)	2.965(3)
C(12)	C(2)	3.1454(7)	C(16)	C(2)	3.3185(7)
C(12)	H(2)	2.739(3)	C(16)	H(1′)	2.800(3)
C(13)	H(53″)	2.986(3)	C(16)	H(51′)	2.857(3)

′) Atoms related by symmetry within the same molecule. — ″) Neighbouring molecule at (x'',y'',z'') = ($0.5 - x$, $0.5 + y$, $0.5 - z$). — ‴) Neighbour at (x''',y''',z''') = ($0.5 + x$, $1.5 - y$, $0.5 + z$).

D. Discussion

The unexceptional value of C(2)−N−C(11) = 120.53(3)° in the dianil **3** is a rather remarkable result (Table 3). It shows that this angle is not easily enlarged by the steric repulsions, even with the close contact between H(2) and the π face of the aromatic C(12) atom (2.739 Å; Table 4). Hence, the enlargement of C−N−C angles in several other imines should result from the π-acceptor influence of *N* substituents in conjugation with the nitrogen lone pair, e.g., acetyl (127°)[28], 10-acridinylium (137°)[31], and 9-fluorenylium (163°)[32]. In the absence of such *N* substituents, the C−N−C angle of 119° in 2,4-bis(4-bromophenylimino)-1,1,3,3-tetramethylcyclobutane[33] may be close to the strain-free value. It is difficult to find other suitable reference structures of aliphatic dialkyl ketone imines without unsaturated or aromatic substituents at the azomethine carbon atom and devoid of bicyclic ring strain, because aldehyde imines[34] would be a poor choice with their hydrogen atom and crystal-induced conformational polymorphism[35], and an early[36] structural analysis of 2-(4-hydroxyphenylimino)propane was rather crude. The numerous structural examples of *N*-metalated imines of di-*tert*-butyl ketone and others do not provide good comparisons.

It appears reasonable to expect that the unknown structure of pinacolone anil (**2a**) will be similar to that of **3**. At a first glance, an (*E*) configuration like that in Figure 3 looks suitable for the direct formation of a 1-azaallyl anion with *syn*-NC conformation. However, (*E*) configurations are poorly suited for α deprotonation, and *anti* deprotonation (with respect to the *N* substituent) is the preferred mode[21,37]. Experimental evidence for the "*syn* effect"[22] has been based on the NC configurations of the products obtained by quenching[22,38], whereas direct spectroscopic measurements revealed only the CC conformations of the 1-azaallyl compounds.

Indeed, neither of the crystal structures of **1** or **4** provides evidence for a strong driving force towards the *syn* conformation. Metalation of a Schiff base may thus be accompanied by profound conformational changes of a starting geometry (like that in **3**). In our structure **1**, such changes consist in 80−90° rotations about both of the N−C bonds and in an aggregation which had not been suspected in 1985[9] within the class of lithiated imines.

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Experimental

Addition Compound of Ether with N-(2,2-Dimethyl-1-methylenepropyl)-N-lithiobenzenamine (**1**): Pinacolone anil[39] (**2a**; 4.29 g, 24.5 mmol) was added under dry nitrogen at −70°C to lithium diisopropylamide (24.6 mmol), freshly prepared from diisopropylamine in anhydrous diethyl ether (25 ml) and *n*-butyllithium in hexane (1.3 M; 20 ml). After 4 h at 25°C, the addition of *n*-butyllithium was repeated at −70°C for total conversion[13] of the starting anil (^{1}H-NMR control), and the mixture was kept at 25°C for ca. 12 h. The solvents and diisopropylamine were then distilled off at 40°C/12 Torr, leaving a copious mass of crystals which dissolved on warming with 10 ml of anhydrous ether under nitrogen. Crystallization started on slow cooling to 25°C and was continued for 4 d. The supernatant liquid was removed with a pipet under streaming nitrogen, and the crystals were washed with a small volume of ether in the same way to yield 2.66 g (42%) of **1** as colourless, transparent platelets. − ^{1}H NMR (THF): as published[13], compare Table 2, with correct signal intensity ratios; (diethyl ether): δ = 1.07 (s, *t*-C_4H_9), 4.33 and 4.77 (AB spectrum with ^2J = 1.0 Hz, 2 β-H), 6.12 (tt, *J* = 7.0 and 2.5 Hz, *p*-H), 6.55 (dm, *J* ≈ 8 Hz, 2 *o*-H), 6.85 (m_c, 2 *m*-H).

$(C_{12}H_{16}LiN \cdot C_4H_{10}O)_2$ $(255.3)_2$ Calcd. C 75.26 H 10.26 N 5.49
Found C 74.31 H 10.05 N 5.90

N-(1-Ethyl-2,2-dimethylpropylidene)benzenamine (**2b**)[40]: Pinacolone anil[39] (**2a**; 920 mg, 5.25 mmol) was deprotonated in diethyl ether as above without solvent distillation. The resulting suspension of **1** was cooled in ice, treated with 1.0 ml of methyl iodide, and left for ca. 12 h. Workup with distd. water and ether gave 860 mg (87%) of the spectroscopically pure anil **2b**. It showed no trace of a ^{1}H-NMR signal for NCH_3 and was not further purified and analyzed because its CH_2 chemical shift was almost the same as that of **3**. − ^{1}H NMR (CCl_4): δ = 0.85 (t, CH_3), 1.20 (s, *t*-C_4H_9), 2.22 (q, CH_2), 6.46 (d, 2 *o*-H), 6.78 (t, 1 *p*-H), 7.10 (t, 2 *m*-H); all ^3J = 7.5 Hz; δ of arom. H larger by 0.2 ppm in $CDCl_3$.

Table 5. Fractional atomic coordinates[a] and equivalent thermal parameters[b] [Å]^2 of **1** with standard deviations in units of the last significant figure in parentheses

Atom	x	y	z	U(eq)
Li	0.5645(2)	0.6037(1)	0.5267(1)	0.0212(5)
O	0.65629(6)	0.75370(5)	0.58620(4)	0.0163(2)
N	0.37960(7)	0.52254(6)	0.54928(4)	0.0128(2)
C(1)	0.5804(1)	0.87357(9)	0.56921(6)	0.0204(3)
C(2)	0.5598(2)	0.9324(1)	0.64825(8)	0.0320(4)
C(3)	0.8133(1)	0.76655(9)	0.62136(7)	0.0235(3)
C(4)	0.8757(1)	0.6422(1)	0.65639(8)	0.0257(4)
C(11)	0.30355(9)	0.62987(7)	0.51450(5)	0.0136(2)
C(12)	0.2965(1)	0.66290(8)	0.42963(6)	0.0162(3)
C(13)	0.2280(1)	0.77196(9)	0.39217(6)	0.0200(3)
C(14)	0.1618(1)	0.85458(8)	0.43555(6)	0.0206(3)
C(15)	0.1667(1)	0.82420(8)	0.51888(6)	0.0206(3)
C(16)	0.2346(1)	0.71594(9)	0.55710(6)	0.0169(3)
C(21)	0.4803(1)	0.5520(1)	0.69956(7)	0.0245(3)
C(22)	0.38484(9)	0.49448(7)	0.63551(5)	0.0145(2)
C(23)	0.28190(9)	0.38928(7)	0.64798(5)	0.0160(3)
C(24)	0.2712(1)	0.38564(9)	0.73959(6)	0.0270(3)
C(25)	0.1275(1)	0.40766(8)	0.58804(6)	0.0240(3)
C(26)	0.3420(1)	0.26172(8)	0.62935(6)	0.0233(3)

[a] Symmetry transformation: (′) = $1 - x$, $1 - y$, $1 - z$. – [b] Equivalent isotropic displacement parameters U(eq) computed as one third of the trace of the orthogonal U_{ij} tensor.

Table 6. Fractional atomic coordinates[a] and equivalent thermal parameters[b] [Å]^2 of **3** with standard deviations in units of the last significant figure in parentheses

Atom	x	y	z	U(eq)
N	0.28740(4)	0.60917(1)	0.31922(2)	0.01347(7)
C(1)	0.52822(5)	0.50129(2)	0.42831(3)	0.01260(8)
C(2)	0.33143(5)	0.53395(2)	0.33556(3)	0.01240(8)
C(3)	0.18342(5)	0.47195(2)	0.25573(3)	0.01369(8)
C(4)	-0.02187(5)	0.51234(2)	0.18010(3)	0.01663(9)
C(5)	0.10335(6)	0.40581(2)	0.34512(3)	0.0191(1)
C(6)	0.32669(6)	0.43291(2)	0.15673(3)	0.0209(1)
C(11)	0.43362(5)	0.66919(2)	0.38209(3)	0.01442(8)
C(12)	0.62790(5)	0.69092(2)	0.32654(3)	0.01660(9)
C(13)	0.76886(5)	0.75096(2)	0.38393(3)	0.01849(9)
C(14)	0.71775(5)	0.79041(2)	0.49615(3)	0.01855(9)
C(15)	0.52225(6)	0.77009(2)	0.55005(3)	0.01806(9)
C(16)	0.37930(5)	0.71020(2)	0.49298(3)	0.01630(9)

[a] Symmetry transformation: (′) = $1 - x$, $1 - y$, $1 - z$. – [b] Equivalent isotropic displacement parameters U(eq) computed as one third of the trace of the orthogonal U_{ij} tensor.

N,N′-[1,4-Bis(1,1-dimethylethyl)butane-1,4-diylidene]bis(benzenamine) (**3**): An aged sample of **1** was treated with cold diethyl ether and the undissolved component recrystallized from cyclohexane, yielding colourless crystals with m.p. 175–177.5°C. – ^{1}H NMR (CDCl$_3$): δ = 0.67 (s, t-C$_4$H$_9$), 2.17 (s, CH$_2$), 6.50 (dm, o-H), 7.1 (m$_c$, m- and p-H).

$C_{24}H_{32}N_2$ (348.5) Calcd. C 82.70 H 9.26 N 8.04
Found C 82.81 H 9.21 N 7.90

X-ray Structure Determinations: The final coordinates are listed in Tables 5 and 6, and analytical details are shown in Table 7. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55392, the names of the authors, and the full literature citation.

A colourless, irregular crystal (split from a large plate) of compound **1** was measured in a glass capillary under argon by graphite-monochromated Mo-K_α radiation, λ = 0.71069 Å.

Table 7. Crystallographic data and refinement parameters of **1** and **3**

	1	**3**
Formula	$(C_{12}H_{16}LiN \cdot C_4H_{10}O)_2$	$C_{24}H_{32}N_2$
Molecular mass	$(255.3)_2$	348.5
Crystal size [mm]	0.20 × 0.23 × 0.45	–
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	9.466(3)	5.993(3)
b [Å]	10.586(2)	16.479(3)
c [Å]	16.449(9)	10.243(1)
α [°]	90	90
β [°]	106.46(3)	96.51(2)
γ [°]	90	90
V [Å^3]	1581	1005
$D_{calcd.}$ [g cm^{-3}] (−156°C)	1.073	1.152
Z	2	2
F(000)	560	380
T [°C]	−156	−156
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Scan	ω/2Θ, NEQ mode[a]	ω/2Θ, NEQ mode[a]
Scan width [° in ω]	1 + 0.35tanΘ	0.9 + 0.35tanΘ
(sinΘ/λ)max [Å^{-1}]	0.90	0.70
hkl range	total	total
Measured reflections	76540	23370
Unique reflections	9767	2924
Observed reflections[b]	2875	2367
Refined parameters	406	182
(LS, F^2)	(matrix 2 blocks)	(full matrix)
R[c]	0.061	0.052
$R_w(F^2)$[d]	0.078	0.064
$\Delta\varrho_{fin}$(max) [e/Å^3]	0.48 (bonds)	0.38 (bonds)

[a] Special scan mode of CAD4 yielding 2 profiles scanned in +ω and −ω directions. – [b] Criteria: **1**: [$F^2 > 5\sigma(F^2)$]; **3**: [$F^2 > 2\sigma(F^2)$]. – [c] $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$. – [d] $R_w(F^2) = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w F_0^4]^{1/2}$; $w = 1/\sigma^2(F_0^2)$.

3 was originally supposed to be the addition compound **1** and was treated in the same way. Both structures were solved by direct methods (MULTAN 76)[41] and refined by full-matrix least-squares methods (X-Ray 76)[42] using weights $1/\sigma^2(F_0^2)$ without absorption and extinction corrections. All hydrogen atoms were taken from the difference maps and introduced with isotropic vibration parameters. Non-hydrogen atoms were refined anisotropically.

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