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Syntheses and Reactions of Some Cyclopropyl-Substituted Imines. Part 1

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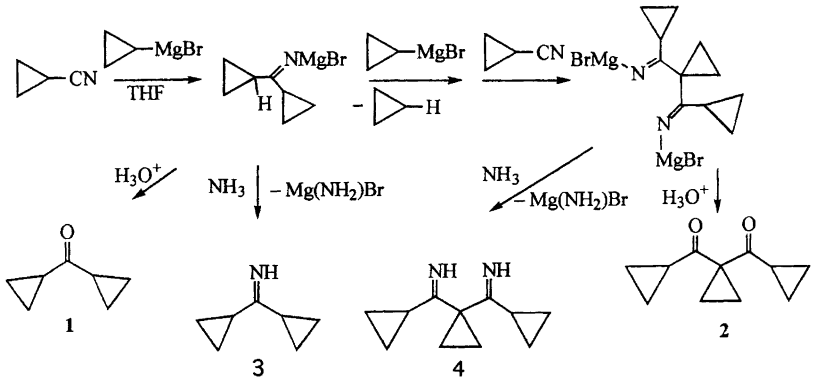
Quenching the reaction solution from cyclopropanecarbonitrile and cyclopropylmagnesium bromide in tetrahydrofuran (THF) with anhydrous NH_3 gave an about equimolar mixture of dicyclopropyl ketimine (**3**) and 1,1-dicyclopropanecarboximidoylcyclopropane (**4**). Reactions of the ketimines **3** and **4** with some nucleophiles are described. Thus, reaction of **4** with malononitrile gave a good yield of 2-amino-3-cyano-5-(3,3-dicyanopropyl)-4,6-dicyclopropylpyridine (**6**). Neat **4**, catalysed by $MgCl_2$, gave a self-condensation product, 1,3,5,7-tetracyclopropyl-2,6,9-triazadispiro{bicyclo[3.3.1]nona-2,6-diene-4,1′:8,1″-dicyclopropane} (**7**), while an equimolar mixture of neat **3** and **4** with catalytic amounts of $MgCl_2$ gave a mixed condensation product, 2′,2′,4′,6′,-tetracyclopropylspiro[cyclopropyl-1,5′-(1′,5′-dihydropyrimidine)] (**8**). Hydrolysis of **4** at medium pH gave a mixture of **7** and the partly hydrolysed **4**: 1-cyclopropanecarbonyl-1-cyclopropanecarboximidoylcyclopropane (**10**). Reaction of **3** with cyclopropylamine gave *N*-cyclopropyldicyclopropyl ketimine (**11**). Gas phase FTIR-spectra of **4** and **10** indicated intramolecular hydrogen bonds. The structures of **7** and **8** were established by single-crystal X-ray analyses. In the bicyclic compound **7** the apical nitrogen atom is pyramidal, making the structure asymmetric (both enantiomers present in the unit cell), as confirmed by solid-state ^{13}C NMR spectroscopy. On the other hand solution ^{13}C NMR shows a high degree of symmetry, explainable by rapid inversion at the apical nitrogen atom.

Recently[1] we have shown that when cyclopropylmagnesium bromide is reacted with cyclopropanecarbonitrile in THF solution, in addition to the expected dicyclopropyl ketone **1**, a dimerization product is formed, which after hydrolysis gives 1,1-di(cyclopropylcarbonyl)-cyclopropane **2** (Scheme 1).

When, instead of hydrolysis, the organometallic compounds were reacted with ammonia, the ketimines **3** and **4** were the sole products. To avoid hydrolysis,[2] the reaction solution was centrifuged, and the ketimines were fractionally distilled from the supernatant (Scheme 1).

Two interesting pieces of information can be deduced from the FTIR spectra (Table 1). Firstly, the C=N stretching frequency for **3** is observed at 1635 cm^{-1}(gas



Scheme 1.

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Table 1. FTIR-spectra of ketimines **3** and **4** in the gas and the liquid phase.[a]

Cpd.	NH str.	CH str. (as)	CH str. (s)	C=N str.	CH_2 (scis.)
3 Gas	3275 (m)	3095 (s)	3018 (s)	1635 (s)	1418 (s)
Neat	3241 (m)	3087 (s)	3006 (s)	1627 (s)	1423 (s)
4 Gas	3265 (w)	3091 (s)	3015 (s)	1624 (s)	1405 (s)
Neat	3247 (m)	3085 (s)	3015 (s)	1622 (s)	1403 (s)

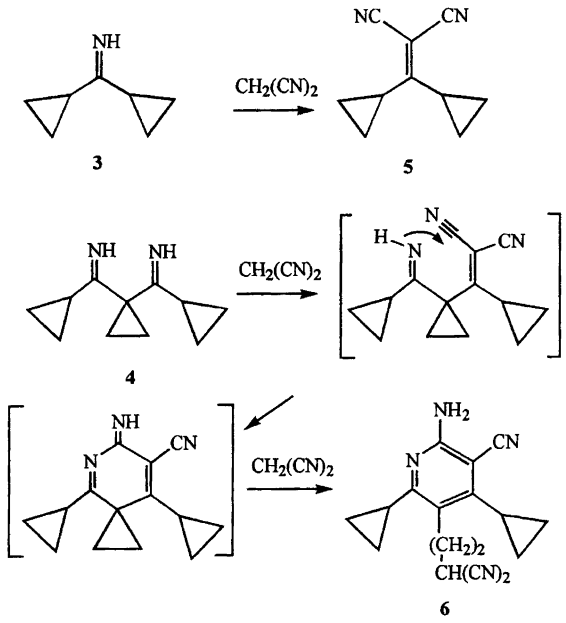
[a] Frequency units, cm^{-1}.

phase), very close to that of the C-unsubstituted methyleneketimine, CH_2=NH, (1638 cm^{-1}, gas phase[3]), somewhat lower than dialkylated ketimines (1640–1646 cm^{-1})[4] and higher than for diphenyl ketimine, $(C_6H_5)_2C$=NH, (1605 cm^{-1}, dilute CCl_4 solution[5]). The frequency lowering is explained by conjugation effects from the phenyl rings.[4] These observations indicate that conjugation between the cyclopropyl rings and the C=N group is negligible, contrary to what is found for the conjugation of a cyclopropane ring with an adjacent C=C bond.[6] Two possible reasons for such behaviour for the ketimines are: (1) less effective overlap in general between the *bent bonds* of the cyclopropane ring and the Π-system of the C=N bond, and/or (2) the two cyclopropane rings are, for steric reasons, twisted out of the plane containing the C=N double bond.

The observed frequency shift upon going from the gas to the condensed phase is as expected. Secondly, the observed frequency shifts for the N–H bond (**3**, 34 cm^{-1}; **4**, 18 cm^{-1}) upon change of phase indicate the presence of intermolecular hydrogen bonds. An expected intramolecular hydrogen bond in the spectrum of **4** is not observed. However, in both the gas phase and the condensed phase spectra of **4** the N–H peak is broader than the corresponding peaks in **3**, thus the inter- and the intra-molecular peaks may be partly overlapping. In general, N–H···N bonds are weaker than the corresponding O–H···O bonds.

In an earlier study a ketimine was found to react quantitatively with malononitrile,[7] thus a mixture of **3** and **4** was made to react likewise (Scheme 2). Ketimine **3** reacted in the expected way to give dicyclopropylmethylidenepropanedinitrile **5**.[8] The diketimine **4**, however, reacted with malononitrile in a way similar to that described earlier,[1] leading to the pentasubstituted pyridine **6**, 2-amino-3-cyano-5-(3,3-dicyanopropyl)-4,6-dicyclopropylpyridine.

In one instance, in the preparation of imines (Scheme 1), the residue after ketimine **3** had been distilled off was left without further purification for several days, after which nicely formed crystals were obtained. High resolution mass spectrometry (HRMS) and NMR spectroscopy indicated that a self-condensation had occurred with expulsion of one mole equivalent of ammonia. Single-crystal X-ray crystallography established the structure as 1,3,5,7-tetracyclopropyl-2,6,9-triazadispiro{bicyclo[3.3.1]nona-2,5-diene-4,1′:8,1″-dicyclopropane} (**7**) [Fig. 1(a)].



Scheme 2.

In another instance, when the supernatant was evaporated after centrifugation, GC-analysis indicated approximately equimolar amounts of ketimines **3** and **4**. The residue was left without purification for several days, after which GC-analysis confirmed that a new compound had been formed. Single crystal X-ray determination confirmed the HRMS, NMR and FTIR spectroscopic analyses in that a cross-condensation of the ketimines **3** and **4** had taken place with expulsion of ammonia to give 2′,2′,4′,6′,-tetracyclopropylspiro[cyclopropyl-1,5′-(1′,5′-dihydropyrimidine)] (**8**) [Fig. 1(b)].

These condensations did not take place when the individual ketimines were purified by distillation before being left for several days, neither equimolar amounts of **3** and **4**, nor pure **4**, respectively. To test the possibility that some Mg compounds [$Mg(NH_2)Br$?], not completely removed during the centrifugation process, could have a catalytic effect, two experiments were run (see the Experimental): one with equimolar amounts of ketimines **3** and **4**, and one with only ketimine **4**, both dissolved in THF with small amounts of $MgCl_2$ added. After three days GC-analyses showed that in the former run only the cross-condensation product **8** was formed in about 35% yield while the self-condensation product **7** was not observed at all. GC-analysis after three days in the latter

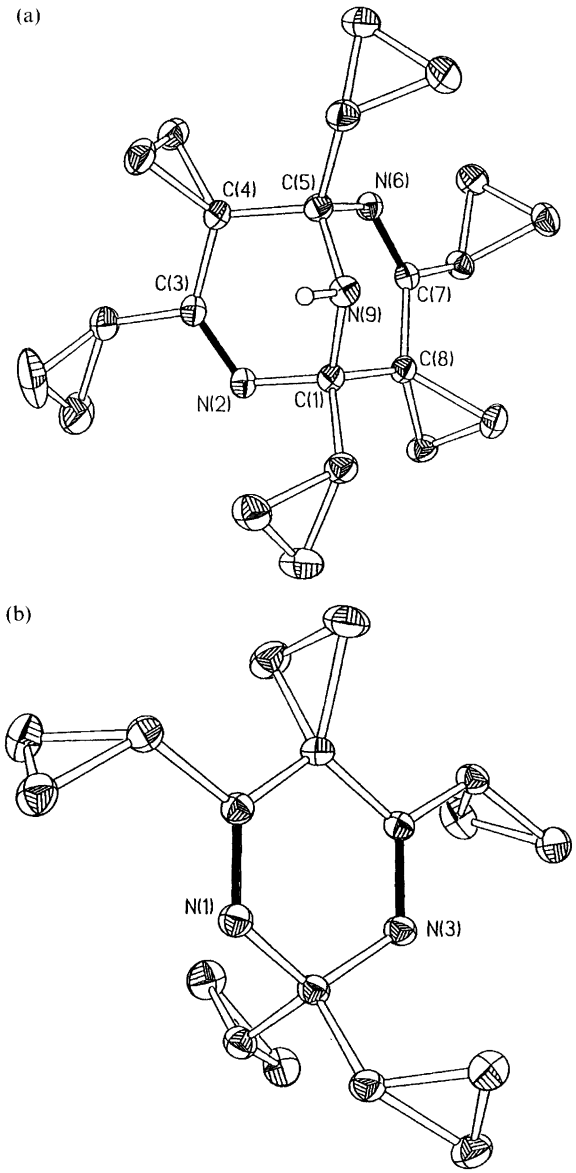
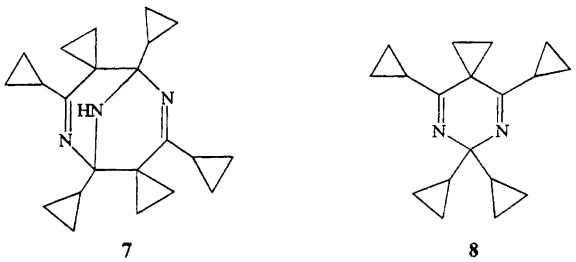


Fig. 1. (a) ORTEP plot of **7**; (b) ORTEP plot of **8**.



7 **8**

run showed that only 18% of **7** had been formed. Steric effects might explain the rate difference in these condensations.

The formation of **7** and **8** is thought to take place by an attack of unchelated **4** or ketimine **3** on the chelated **4** (Scheme 3).

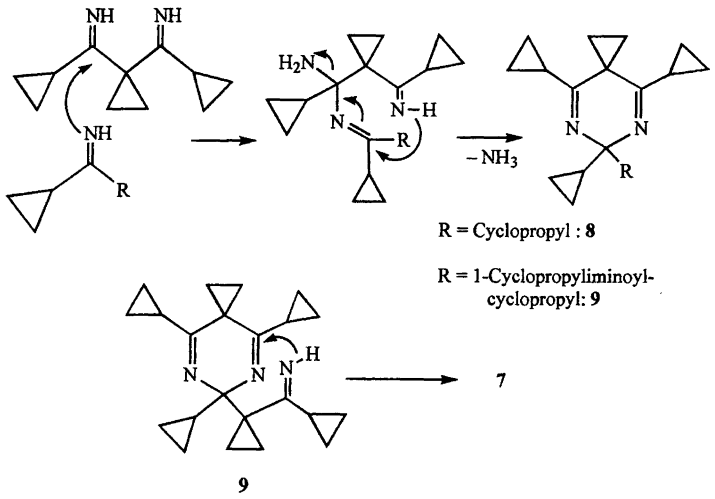
The crystal structure of **7** [Fig. 1(a)] shows that the molecule does not contain any symmetry elements. On the other hand, in the high resolution ^{13}C NMR spectrum of **7** in non-polar solvents ($CDCl_3$, CD_2Cl_2 or C_6D_6) only eleven resonance lines (for 22 carbon atoms) are present, showing some sort of symmetry. Solid state ^{13}C NMR shows that several of these eleven lines are split. These conflicting observations may be explained as a result of nitrogen inversion involving N9. In the solid state this nitrogen atom is pyramidal with the hydrogen pointing towards C3 making this nitrogen chiral. Both enantiomers are present in the unit cell. In each enantiomer the eight-membered ring is asymmetric as indicated by the different bond lengths of the transannular bonds, e.g., C3–C4 [1.5082(14) Å] and C7–C8 [1.4959(13) Å]. In solution the nitrogen inversion (the 'racemization') is faster than the NMR timescale. Solubility problems limited NMR observation below −110 °C. Above this temperature no broadening of the resonance line for C3 and C7 (170.3 ppm) was observed,† thus these atoms will be in the same (averaged) magnetic surroundings in solution, while in solid state the split is ≈1.4 ppm. This split is the largest observed, probably since H9 in each enantiomer will be closest to either C3 or C7. The splittings observed for the other ring carbon atom pairs are smaller C4/C8 ≈ 0.8 ppm, C1/C5 ≈ 0.5 ppm.

Preliminary experiments have shown that the two ketimines **3** and **4** react with water at different rates. In tetrahydrofuran (THF), containing excess water with some ammonium chloride added, and using the fractional half-life method on an equimolar mixture of **3** and **4**, ketimine **3** is hydrolysed approximately five times faster that **4**. From **3** dicyclopropyl ketone **1** is the product, while **4** reacted in a more complicated manner. The products obtained were the partly hydrolysed ketimine 1-cyclopropanecarbonyl-1-cyclopropanecarboximidoyl-cyclopropane **10** together with the condensation product **7**. The reaction of **4** in aqueous acetonitrile, with ammonium chloride added, was then studied separately and monitored gas chromatographically (Fig. 2).

On a qualitative scale, protonation of **4** has an effect on the electrophilicity of the ketimine similar to chelation by magnesium chloride. Water and unprotonated **4** then act competitively as nucleophiles to form the reaction products (Scheme 4). An interesting observation is that protonation seems to increase the rate of formation of the self-condensation product (Fig. 2) compared with the $MgCl_2$-catalysed reaction, see above.

When, instead of ammonium chloride, equimolar amounts of trifluoroacetic acid were used to increase the acidity, the consumption of the starting material was much faster and the outcome was somewhat different:

† $\nu_{1/2}$ increases from 0.03 Hz at 0 °C to 0.06 Hz at −100 °C; this increase is probably only a result of an increase in viscosity upon cooling. Thus it is not expected that coalesence will occur above the temperature limit of the existing NMR-instruments, −150 °C.



Scheme 3.

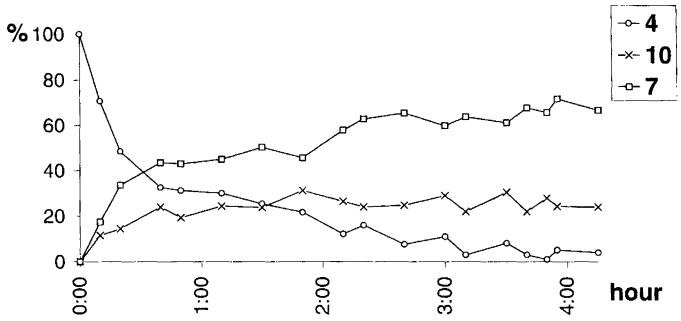
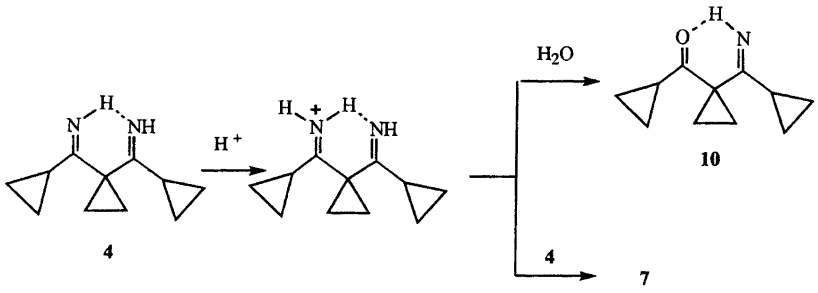


Fig. 2. Reaction of **4** in aqueous acetonitrile.



Scheme 4.

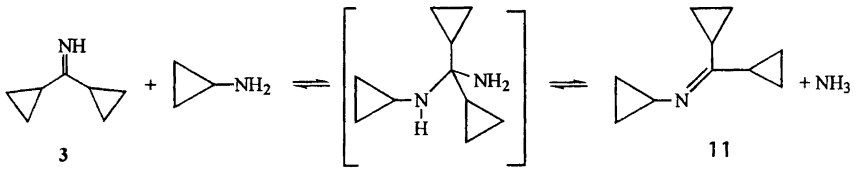
the yield of **7** was reduced and instead of the keto-ketimine **10**, the hydrolysis was complete to give the diketone **2**. The reason for the reduced yield of **7** is most likely that increased acidity reduces the effective concentration of unprotonated **4**. This observation parallels the decreased rate of addition of amino nucleophiles to carbonyl groups (e.g., in oxime formation) at low pH.[9] Thus hydrolysis of the starting material becomes more competitive.

Compound **10** could not be obtained in a pure state by any type of chromatography, therefore its structure was established by combined use of HRMS, GC–FTIR, GC–MS and subtraction programs in NMR-spectroscopy, see Experimental. The gas-phase FTIR spectrum contained a very low frequency N–H band (2972 cm^{-1}) and a rather low C=N stretching frequency band (1602 cm^{-1}) probably due to a strong intramolecular N–H···O hydrogen bond.

The primary amine cyclopropylamine reacts with ketimine **3** in a straightforward way, presumably through a tetrahedral intermediate from which the lowest boiling amine normally becomes the preferred nucleofuge (Scheme 5).[2,10]

Experimental

General. Melting points are uncorrected. Boiling points (uncorrected) were determined using a Mettler FP1



Scheme 5.

apparatus. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using an attenuated total reflectance (ATR) ZnSe-plate for solid and liquid samples, gas phase spectra were recorded using a Varian 3300 gas chromatograph coupled to the inlet of the above FTIR instrument, ultraviolet spectra on a Shimadzu UV-260 spectrophotometer and mass spectra on a Fison Instrument VG ProSpec Q. High resolution NMR spectra (^{1}H and ^{13}C) were recorded on Bruker Spectrospin Avance DPX 300 and DRX 500 spectrometers, and solid state ^{13}C NMR spectra on a Bruker Spectrospin Avance DMX 200 spectrometer. NMR peak assignments were made using 2-D spectroscopy or other suitable pulse programs.

All solvents used were dried according to literature recommendations.[11]

Reaction of cyclopropanecarbonitrile with cyclopropylmagnesium bromide in THF and quenching with NH_3. To a solution of cyclopropylmagnesium bromide made from magnesium (0.80 g, 33 mmol) and bromocyclopropane (3.60 g, 30 mmol) in THF (20 ml) was added dropwise cyclopropanecarbonitrile (1.40 g, 20 mmol) in THF (15 ml). The reaction was refluxed for 5 h, after which anhydrous NH_3 was passed into the reaction mixture for 1 h. After centrifugation and evaporation of the solvent, the clear liquid (1.6 g) was fractionally distilled.

Dicyclopropyl ketimine (**3**): (0.5 g, 4.6 mmol), b.p. 74 °C/25 mmHg. Anal. (HRMS): Found 109.0859. Calc. for $C_7H_{11}N$: 109.0891. FTIR: ν_{max} 3247 (w), 3087 (m), 3006 (s), 1619 (s), 1422 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.05 (1 H, s), 1.4–1.3 (2 H, m), 0.7–0.6 (8 H, m). ^{13}C NMR ($CDCl_3$): δ 184.6, 17.0, 7.2. MS [EI, 70 eV: *m/z* (% rel. int.)]: 109 (7 $[M]^{+\cdot}$), 108 (70, $[M-H]^+$), 94 (86), 68 (100).

1,1-Di(cyclopropanecarboximidoyl)cyclopropane (**4**): (0.8 g, 4.5 mmol), b.p. 49.5 °C (0.0112 mmHg). Anal. (HRMS): Found 176.1305. Calc. for $C_{11}H_{16}N_2$: 176.1313. FTIR: ν_{max} 3247 (m), 3085 (m), 1622 (s), 1403 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.64 (2 H, s), 1.60 (2 H, quintet, *J* 6.4 Hz), 1.18 (4 H, s), 0.82 (8 H, d, *J* 6.7 Hz). ^{13}C NMR ($CDCl_3$): δ 182.0, 39.5, 15.5, 12.4, 9.0. MS [EI, 70 eV: *m/z* (% rel. int.)]: 175 (7, $[M-H]^+$, 147 (19), 108 (68), 94 (100).

Reaction of ketimines **3** *and* **4** *with malononitrile.* To an about equimolar (GC) mixture (1.6 g) of imines **3** and **4** was added malononitrile (1.3 g, 20 mmol) dissolved in THF (20 ml). The reaction was refluxed for 1 h, after which the solvent was evaporated off to give a dark oil. Column chromatography on an SiO_2 column (eluent: 5:1 CH_2Cl_2–EtOAc) gave two products eluting in the following order.

Dicyclopropylmethylenepropanedinitrile (**5**):[8] 0.6 g (3.8 mmol), m.p. 43–44 °C. FTIR: ν_{max} 3093 (w), 3019 (m), 2225 (s, CN), 1556 (s). ^{1}H NMR ($CDCl_3$): δ 1.8–1.7 (2 H, m), 1.3–1.1 (8 H, m).^{13}C NMR ($CDCl_3$): δ 185.8, 112.8, 81.3, 16.8, 10.2. MS [EI, 70 eV: *m/z* (% rel. int.)]: 158 (45, $[M]^{+\cdot}$), 157 (23, $[M-H]^+$), 143 (73), 130 (62) 116 (100).

2-Amino-3-cyano-5-(3,3-dicyanopropyl)-4,6-dicyclopropylpyridine (**6**): 0.7 g (2.4 mmol), m.p. 141–143 °C. Anal. (HRMS): Found 291.1484. Calc. for $C_{17}H_{17}N_5$: 291.1488. FTIR: ν_{max} 3486 (m), 3375 (s), 3217 (w), 3090 (w), 3008 (m), 2910 (m), 2256 (w), 2210 (s), [1613 (s), 1559 (s) (pyridine quadrant stretch)],[12] 1431 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.96 (2 H, s), 3.90 (1 H, t, *J* 6.3 Hz), 3.3–3.2 (2 H, m), 2.3–2.2 (2 H, m), 2.0–1.9 (1 H, m), 1.9–1.8 (1 H, m), 1.3–0.8 (8 H, m). ^{13}C NMR ($CDCl_3$): δ 164.2, 158.6, 153.3, 122.4, 116.8, 112.3, 90.0, 30.6, 24.1, 22.5, 13.7, 13.4, 10.7, 8.0. MS [EI, 70 eV: *m/z* (% rel. int.)]: 291 (53), 290 (15), 226 (25), 212 (62), 198 (45).

Self-condensation of diimine **4**. To neat **4** (0.18 g, 1 mmol) was added anhydrous $MgCl_2$ (5 mg, 52.5 μmol). After 7 days, white crystals (0.13 g, 0.4 mmol) of *1,3,5,7-tetracyclopropyl-2,6,9-triazaspiro{bicyclo[3.3.1]nona-2,6-diene-4,1':8,2"-dicyclopropane}* (**7**) were formed, which were washed with pentane, m.p. 110–111 °C. X-Ray crystallography, see below. Anal. (HRMS): Found 335.2365. Calc. for $C_{22}H_{29}N_3$: 335.2361. FTIR: ν_{max} 3247 (w), 3086 (m), 3004 (s), 1637 (s), 1413 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.64 (1 H, br s), 1.4–1.3 (2 H, m), 1.1–1.0 (4 H, m), 1.0–0.9 (4 H, m), 0.7–0,6 (4 H, m), 0.6–0.5 (4 H, m), 0.5–0.4 (4 H, m), 0.3–0.2 (2 H, m), 0.2–0.1 (2 H, m), −0.1 to −0.2 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 170.3 (C3/C7), 66.8 (C4/C8), 29.6 (C1/C5), 16.7, 10.8, 10.4, 9.2, 8.3, 7.5, 0.4, −2.5. MS [EI, 70 eV: *m/z* (% rel. int.)]: 335 (14, $[M]^{+\cdot}$), 294 (32), 268 (31), 253 (94), 239 (70), 227 (100).

Mixed condensation of monoimine **3** *and diimine* **4**. Neat **3** (0.11 g, 1 mmol) and **4** (0.18 g, 1 mmol) were mixed and anhydrous $MgCl_2$ (5 mg, 52.5 μmol) was added. After 3 days white crystals (0.23 g, 0.85 mmol) of *2',2',4',6',-tetracyclopropylspiro[cyclopropane-1,5'-(1',5'-dihydropyrimidine)]* (**8**), were formed, which were washed with pentane, m.p. 49.5–50.0 °C. X-Ray crystal-

lography, see below. Anal. (HRMS): Found 268.1964. Calc. for $C_{18}H_{24}N_2$: 268.1940. FTIR: ν_{max} 3083 (m), 3004 (s), 1678 (s), 1406 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.40 (4 H, s), 1.3–1.2 (2 H, m), 1.0–0.9 (2 H, m), 0.8–0.7 (4 H, m), 0.6–0.5 (4 H, m), 0.2–0.1 (8 H, m). ^{13}C NMR ($CDCl_3$): δ 165.4, 73.3, 22.9, 22.3, 13.1, 10.5, 7.5, −0.2. MS [EI, 70 eV: *m/z* (% rel. int.)]: 268 (95 $[M]^{+\cdot}$), 227 (100), 172 (43), 160 (62).

Reaction of ketimine **4** *with water.* (*A*) **4** (0.25 g, 1.4 mmol) was dissolved in acetonitrile (10 ml), and ammonium chloride (0.3 ml, 1 M) was added. The reaction was then monitored by gas chromatography (Fig. 2). After about 4 h most of the starting ketimine had reacted. Unfortunately, the keto-ketimine **10** (≈25%) could not be obtained in a pure state. However, HRMS, GC–FTIR, GC–MS and subtraction routines in NMR spectroscopy gave all the pertinent parameters necessary to verify the structure proposed. Anal. (HRMS): Found 177.1132. Calc. for $C_{11}H_{15}NO$: 177.1154. FTIR (gas phase): ν_{max} 3102 (w), 3020 (m), 2972 (w), 1700 (s), 1602 (m), 1379 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.91 (1 H, br s), 2.1–2.0 (1 H, m), 1.7–1.6, (1 H, m), 1.3–1.2 (2 H, m), 1.1–1.0 (2 H, m), 0.9–0.7 (8 H, m). ^{13}C NMR ($CDCl_3$): δ 207.0, 182.5, 42.1, 18.5, 17.7, 15.7, 11.6, 9.9. GC–MS [EI, 70 eV: *m/z* (% rel. int.)]: 177 (2 $[M]^{+\cdot}$), 176 (10 $[M-H]^+$), 162 (12), 149 (52 $[M-CO]^{+\cdot}$), 134 (49), 69 (80 $[C_3H_4CO]^+$), 41 (100 $[C_3H_5]^+$).

In addition, about 65% of the self-condensation product **7** was produced.

(*B*) **4** (0.18 g, 1 mmol) was dissolved in acetonitrile (10 ml) and then water (0.3 ml) containing 1 mmol TFA was added. After 1 h, the solution was analysed by GC, which showed ≈15% of **7** and ≈75% of the diketone **2**.

Reaction of **3** *with cyclopropylamine.* **3** (0.12 g, 1 mmol) was dissolved in THF (5 ml) and then cyclopropylamine (0.1 ml, 1.5 mmol, Fluka) was added. The solution was left at room temperature for 15 h, after which the solvent was removed to give 0.14 g (94%) *N-cyclopropyldicyclopropyl ketimine* **11**. Anal. (HRMS): Found 149.1210. Calc. for $C_{10}H_{15}N$: 149.120450. FTIR: ν_{max} 3089 (m), 3006 (s), 1632 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.1–3.0 (1 H, m), 2.0–1.9 (1 H, m), 1.1–1.0 (1 H, m), 0.9–0.4 (12 H,m). ^{13}C NMR ($CDCl_3$): δ 171.6, 31.9, 13.1, 12.6, 8.2, 6.5, 5.5. MS [EI, 70 eV: *m/z* (% rel. int.)]: 149 (5 $[M]^{+\cdot}$), 148 (11 $[M-H]^+$), 121 (44), 120 (100), 108 (32), 79 (59).

X-Ray crystallography. X-ray data were collected on a Siemens SMART CCD diffractometer[13] using graphite monochromated Mo Kα radiation. Data collection method: (ω-scan, range 0.6°, crystal-to-detector distance 5 cm; further information is given in Table 2. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[13] Absorption corrections were applied by the use of the SADABS program.[14]

Table 2. Crystal data and structure refinement.

Identification code	**7**	**8**
Empirical formula	$C_{22}H_{29}N_3$	$C_{18}H_{24}N_2$
M.p./°C	110–111	49.5–50.0
Formula weight	335.48	268.39
T/K	150(2)	150(2)
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	$a=9.384(1)$ Å	$a=9.526(1)$ Å
	$b=10.940(1)$ Å	$b=16.086(1)$ Å
	$c=17.856(1)$ Å	$c=9.672(1)$ Å
	$\beta=97.01(1)°$	$\beta=92.71(1)°$
Volume, *Z*/Å^3	1819.34(8), 4	1480.43(6)
D_{calc}/mg m^{-3}	1.225	1.204
Absorption coefficient/mm^{-1}	0.073	0.071
F(000)	728	584
Crystal size/mm	0.4 × 0.3 × 0.15	0.15 × 0.25 × 0.10
θ-range for data collection	2.19–33.34°	2.46–40.27°
Limiting indices	$-14\leqslant h\leqslant 14$,	$-17\leqslant h\leqslant 16$,
	$-16\leqslant k\leqslant 15$,	$-29\leqslant k\leqslant 28$,
	$-26\leqslant l\leqslant 27$	$-17\leqslant l<17$
Reflections collected	21080	22029
Independent reflections	6810 [*R*(int) = 0.037]	8708 [*R*(int) = 0.015]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6810/0/342	8708/0/181
Goodness-of-fit on F^2	1.05	1.15
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.053$, $wR_2=0.127$	$R_1=0.046$, $wR_2=0.117$
R indices (all data)	$R_1=0.069$, $wR_2=0.138$	$R_1=0.050$, $wR_2=0.122$
Largest diff. peak and hole	0.49 and −0.30 eÅ^{-3}	0.45 and −0.26 eÅ^{-3}

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\approx 2 \times 10^3$) for **7** and **8**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
7				
N(2)	6851(1)	7204(1)	492(1)	18(1)
N(6)	8340(1)	4810(1)	1327(1)	18(1)
N(9)	7805(1)	6794(1)	1837(1)	18(1)
C(1)	6542(1)	6886(1)	1258(1)	16(1)
C(3)	8142(1)	7121(1)	330(1)	19(1)
C(4)	9389(1)	6628(1)	856(1)	18(1)
C(5)	8907(1)	6020(1)	1557(1)	17(1)
C(7)	6980(1)	4632(1)	1192(1)	17(1)
C(8)	5869(1)	5607(1)	1217(1)	17(1)
C(10)	5581(1)	7878(1)	1517(1)	21(1)
C(11)	5800(1)	9195(1)	1307(1)	27(1)
C(12)	4458(1)	8527(1)	981(1)	30(1)
C(13)	8441(1)	7627(1)	−413(1)	28(1)
C(14)	7274(2)	8192(2)	−951(1)	50(1)
C(15)	8351(2)	8988(2)	−508(1)	53(1)
C(16)	10787(1)	7364(1)	918(1)	26(1)
C(17)	10703(1)	6140(1)	538(1)	24(1)
C(18)	10119(1)	5849(1)	2207(1)	23(1)
C(19)	11104(1)	4754(1)	2242(1)	31(1)
C(20)	10014(1)	4869(1)	2788(1)	31(1)
C(21)	6475(1)	3341(1)	1050(1)	20(1)
C(22)	6630(1)	2494(1)	1731(1)	26(1)
C(23)	7550(1)	2316(1)	1114(1)	26(1)
C(24)	4358(1)	5428(1)	811(1)	21(1)
C(25)	4621(1)	5302(1)	1652(1)	23(1)
8				
N(1)	2670(1)	1066(1)	10128(1)	16(1)
C(2)	2675(1)	917(1)	8627(1)	15(1)
N(3)	2682(1)	1636(1)	7706(1)	16(1)
C(4)	2413(1)	2360(1)	8172(1)	14(1)
C(5)	2192(1)	2532(1)	9661(1)	15(1)
C(6)	2430(1)	1795(1)	10585(1)	15(1)
C(7)	1351(1)	401(1)	8274(1)	18(1)
C(8)	621(1)	427(1)	6860(1)	24(1)
C(9)	−63(1)	814(1)	8083(1)	26(1)
C(10)	3964(1)	380(1)	8394(1)	17(1)
C(11)	5356(1)	764(1)	8081(1)	21(1)
C(12)	4530(1)	281(1)	6976(1)	22(1)
C(13)	2204(1)	3057(1)	7158(1)	17(1)
C(14)	2539(1)	2926(1)	5671(1)	23(1)
C(15)	1036(1)	2942(1)	6049(1)	25(1)
C(16)	994(1)	3127(1)	9980(1)	25(1)
C(17)	2471(1)	3410(1)	10223(1)	26(1)
C(18)	2299(1)	1910(1)	12111(1)	19(1)
C(19)	2286(1)	1160(1)	13040(1)	22(1)
C(20)	939(1)	1614(1)	12705(1)	25(1)

The structures were determined and refined using the SHELXTL program package.[15] The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen positions were calculated from geometrical criteria and refined with isotropic thermal parameters. Final figures of merit are included in Table 2. Positional and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 3. ORTEP drawings for **7** and **8** are given in Fig. 1(a) and 1(b), respectively. Lists of structure factors, anisotropic thermal parameters, hydrogen parameters, and a complete list of bond lengths and bond angles may be obtained from C.R. upon request.

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